BY-PRODUCTS OF THE NITRATION OF TOLUENE.

BY

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ABBREVIATIONS.

A.	Liebig's Annalen der Chemie.
A. Chim. Phys.	Annales de Chimie et de Physique.
Amer. Inst. Chem. Eng.	American Institute of Chemical Engineers.
Arch. pharm.	Archiv der Pharmazie.
Ber.	Berichte der deutschen chemischen Gesellschaft.
B. P.	British Patent.
Berz. Jahresb.	Berzelius Jahresbericht.
Bull. Soc. Chim.	Bulletin de la Société Chimique de France.
C.	Chemisches Zentralblatt.
Chem. & Met. Eng.	Chemical and Metallurgical Engineering.
Chem. Rev.	Chemical Reviews.
Ch. Z.	Chemiker-Zeitung.
Chim. et Ind.	Chimie et Industrie.
Comp. Rend.	Comptes Rendus des séances de l'académie des sciences.
Frdl.	Friedländers' Fortschritte der Teerfarbenfabrikation.
Gazzetta (Gaz.)	Gazzetta chimica italiana.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
J.A.C.S.	Journal of the American Chemical Society.
J.Chem.Ind.	Journal of Chemical Industry, Moscow.

J.C.S.	Journal of the Chemical Society.
J. Franklin Inst.	Journal of the Franklin Institute.
J.Gen.Chem.U.S.S.R.	Journal of the general chemical Society, U.S.S.R.
J. Phys. Chem.	Journal of Physical Chemistry.
J. Prakt Chem.	Journal für praktische Chemie.
J.R.T.C.	Journal of the Royal Technical College, Glasgow.
J. Russ. Phys. Chem. Soc.	Journal of the Russian physical-chemical Society.
J.S.C.I.	Journal of the Society of Chemical Industry.
Mem. Poudres.	Mémorial des poudres.
Monatsh.	Monatshefte für Chemie.
Pharm. Weekblad.	Pharmazeutisch weekblad voor Nederland.
Phys. Zeit.	Physicalische Zeitschrift.
Proc. Royal Soc.	Proceedings of the Royal Society, London.
U.S.	United States of America patent.
R.	Recueil des travaux chimique des Pays-Bas.
Z.	Zeitschrift für Chemie.
Z. anal. chem.	Zeitschrift für analytische Chemie.
Z. angew. chem.	Zeitschrift für angewandte Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische Chemie.
Z. Phys. Chem.	Zeitschrift für physikalische Chemie.

I N D E X .

PART IV.

ACCELERATION OF NITRATION PROCESS

I N T R O D U C T I O N.

CHAPTER I.

HISTORICAL.

Nitration processes involving the use of mixtures of sulphuric and nitric acids have assumed paramount importance because of the use of nitro compounds as dye intermediates, and of polynitro compounds as explosives.

As far as can be ascertained, the first aromatic nitration was carried out in 1834 by Mitscherlich (Berz. Jahresb. 15,429), who prepared nitrobenzene and nitrotoluene by acting upon benzene and toluene respectively with fuming nitric acid. Collas, in France was the first to introduce nitrobenzene into commerce under the name of "essence of mirbane", employing it as a scent for soap and as a bitter almond flavouring. In 1847, Mansfield (J.C.S. 1848,1,244) took out a patent for the manufacture of nitrobenzene from coal tar benzene. It was not until 1856, however, that it was produced in quantity at Kennington by Messrs. Simpson, Maule and Nicholson, who used an all-glass apparatus. Afterwards, when the scale of manufacture was increased, cast iron vessels equipped with mechanical stirrers were introduced.

In 1865, Jaworsky (Z. 1865,1,223) and latter in 1869 Rosenstiehl (Z. 1869,5,190) undertook the nitration of /

toluene with more success. In that same year, Beilstein and Kuhlberg (A. 1870,155,1) isolated for the first time several isomers of mono and dinitrotoluene, by nitrating toluene with nitric acid, and with nitric and sulphuric acids of various concentrations. Trinitrotoluene (T.N.T.) was prepared in 1863 by Wilbrand (A. 1863,128,178) and in 1869 by Beilstein and Kuhlberg (A. 1870,155,27). Paul Hepp in 1880 produced particularly pure T.N.T. from ortho and para nitrotoluene (Sidgwick's Org. Chem. Nitrogen p. 228).

The aliphatic nitro compounds were not discovered until long after their aromatic analogues were well known. Members of this class were first prepared by Victor Meyer in 1872 (Ber. 1872,5,404) and by Kolbe shortly afterwards. With the higher aliphatic hydrocarbons, nitro compounds can be produced by the action of fuming nitric acid. For the lower hydrocarbons, however, reaction was brought about by the use of silver nitrite on the corresponding iodide. Such a process is not referred to as nitration which is usually confined to the action of mixed acid. Of late, vapour phase nitration has tended to simplify the preparation of aliphatic nitro compounds.

Although explosives in the form of black powder had been in use before the thirteenth century, little advance was made in the discovery of organic explosives /

explosives until 1846. In that year two German scientists, Schönbeim and Böttger (Archives des Science Physique et Naturelles, 1846) simultaneously discovered nitrocellulose, but though it was useful as a high explosive, e.g. in torpedoes, it could not be used as a propellant. In 1886 however, the French physicist, Vieille, of École polytechnique, Paris, showed that if a mixture of gun cotton and soluble nitro cotton was made into a paste with ether and alcohol, the gelatinised material left after removal of the ether and alcohol, burned smoothly and rapidly and could be used as a propellant. This was the first smokeless powder to be used for military purposes.

The Italian experimenter, Sobrero (A. 1847,64, 398) discovered nitroglycerine in 1847. It was first manufactured on a commercial scale in 1862 by Nobel but it was found difficult to handle on account of its great sensitiveness to shock. In 1866 however, Nobel (B.P. 1345) discovered that, if liquid nitroglycerine was mixed with Kieselguhr, it could be transported and handled with comparative freedom from danger. This mixture was introduced commercially in 1867 under the name of dynamite. In 1875 Nobel introduced a new type of explosive by mixing nitro cotton with nitroglycerine to give blasting gelatine (B.P. 4179). In 1889 a mixture /

mixture of gun cotton and nitroglycerine with a small amount of mineral jelly was introduced into England under the name of cordite.

The formation of picric acid was observed by Woulfe in 1771 when he was treating silk with nitric acid. Twelve years later it was independently discovered by Hausserman (J.Phys.Chem. March 1788) when he treated indigo with nitric acid. Welter (A.Chim.Phys. 1795,(i), 29,301) in 1795 manufactured it by the action of nitric acid on silk, but Laurent in 1841 (A.Chim.Phys. 184,(iii), 3,221) was the first to produce it by nitrating phenol and dinitrophenol, thereby proving that the well known picric acid was identical with trinitrophenol. In 1871 Sprengel (B.P. 921 and 2642, also J.C.S. 1873,26,803) pointed out that picric acid could be detonated. No practical use was made of this fact until about 1886 when Turpin (B.P. 15089) proposed to use it for filling high explosive shells. Picric acid soon became the chief high explosive and it was widely used in this country until 1914. The French government adopted it under the name of Melinite, but later it was known by other names such as Lyddite. Due to its acidic nature and the ease with which it formed salts sensitive to shock, many serious explosions occurred which finally resulted in the almost complete replacement of picric acid by T.N.T.

T.N.T., although free from these disadvantages, requires the use of highly concentrated acids which before

before 1900 were relatively costly. In that year, however, the Badischen - Anilin und Sodafabrik solved the problem of manufacturing concentrated sulphuric acid by the contact process, which quickly reduced the cost of highly concentrated sulphuric acid and incidentally made the manufacture of indigo possible by the oxidation of naphthalene. In 1901, T.N.T. was unreservedly adopted by the explosive industry, and as a high explosive for military purposes it came into prominence during the Great War of 1914-1918. In this country, it was not until 1915, however, that the first government factory for its manufacture was erected at Oldbury. Mixed with ammonium nitrate it was used as a filling for shells under the name of amatol.

With the outbreak of war in 1939, the demand for explosives, chiefly T.N.T., was naturally of paramount importance. Moreover, since the last war, continuous nitration, with its many advantages, has tended to displace the old batch process. In this connection, Bowden and Smith (B.P. 381,291) in 1932 took out a patent for the continuous nitration of M.N.T. to T.N.T. It consisted of a series of nitrators and separators, the latter being on a slightly higher level /

level than the former to permit of gravity flow. The nitrators were connected near the top by means of shallow channels so that in the event of one being overfull, the surplus flowed to the nitrators on either side. Raising of the slurry from nitrator to separator was carried out by air or other lifts. The sulphuric acid and nitrobody flow was counter-current and further nitration was effected by the addition of relatively small quantities of nitric acid at a number of intermediate stages with a view to effecting controlled nitration at each stage.

The result of this recent introduction is that many problems peculiar to continuous operation have arisen requiring investigation. It is the purpose of this work to investigate some of the losses and difficulties associated with T.N.T. manufacture.

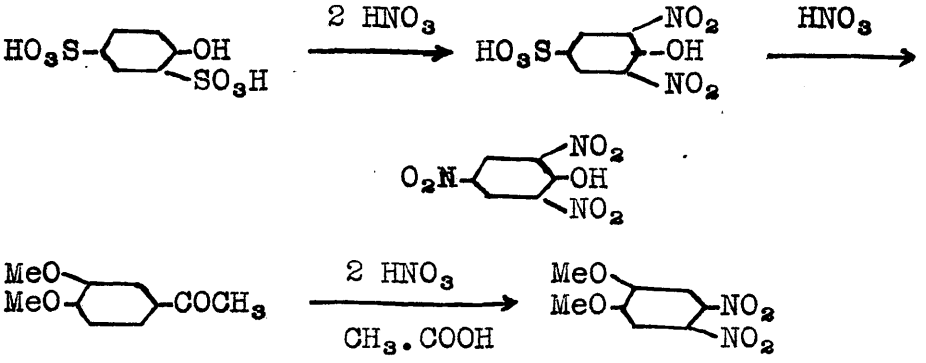
CHAPTER 2.

NITRATION AND THE STRUCTURE OF SOME NITRATING AGENTS.

Nitration is the irreversible process by which the union of a nitro group to a carbon atom is effected. Generally it is a hydrogen atom that is replaced.

$$XH + HO.NO_2 = X.NO_2 + H_2O$$

In a few cases, however, not a hydrogen atom but a sulphonic or an acetyl group is replaced



Nitration is a reaction relating more particularly to aromatic compounds; in this case, nuclear nitration is more common (though side chain nitration is also possible). Aliphatic compounds, however, are also capable of undergoing nitration under special conditions e.g. vapour phase nitration (Groggins, Unit Processes in Org. Chem. pp. 3, 50; Ind.Eng.Chem., 1938, 30, 64 and 67).

Various /

Various nitrogen containing compounds are employed as nitrating agents and some of these with their structures are listed below.

STRUCTURE OF SOME NITRATING AGENTS.

Nitrating agent	Remarks	Structure
Nitric acid	pseudo acid	$HO.N\begin{matrix}O\\ \searrow O\end{matrix}$
Nitric acid anhydride	mixed anhydride	$O_2N.O.NO_2$
Nitro sulphuric acid	" "	$HO.SO_2.O.NO_2$
Acetyl nitrate	" "	$CH_3.CO.O.NO_2$
Benzoyl nitrate	" "	$Ph.CO.O.NO_2$
Diacetyl-o-nitric) acid)	from nitrates and glacial acetic acid	$(CH_3.COOH)_2HO.NO_2$ or $(CH_3.CO)_2N(OH)_3$

From a study of the above it can be seen that these nitrating agents

(1) contain a nitro group as part of a labile complex. (generally the nitro group is held by a shared oxygen atom).

(2) possess similarity in structure to nitric acid esters e.g. they tend to be covalent.

(3) possess pronounced auxiliary valency or free energy for forming addition compounds. (Groggins, Unit Processes in Org. Chem. p. 15).

NITRO GROUP :

There /

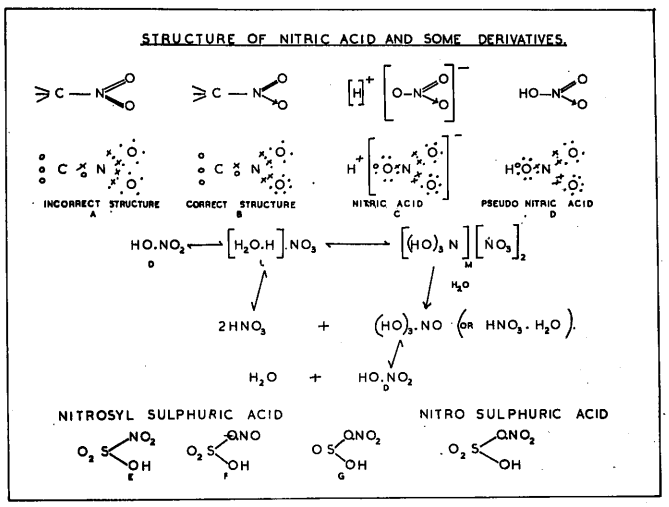
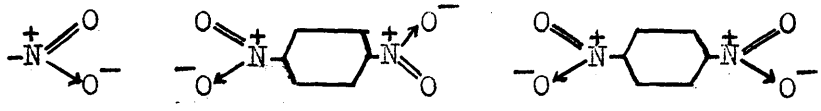

STRUCTURE OF NITRIC ACID AND SOME DERIVATIVES.
INCORRECT STRUCTURE
A
CORRECT STRUCTURE
B
NITRIC ACID
C
PSEUDO NITRIC ACID
D
HO.NO2
O
H2O.H
L
NO3
(HO)3 N
M
NO3
2
H2O
2HNO3
+
(HO)3.NO
(OR HNO3. H2O)
H2O
+
HO.NO2
D
NITROSYL SULPHURIC ACID
NITRO SULPHURIC ACID
E
F
G

FIG. 1.

There has been a great deal of controversy over the correct structure for a nitro group. Structure A (fig.1) shows nitrogen with a covalency maximum of five and with ten electrons in the outer shell and for these reasons it is not acceptable. The formula satisfying modern atomic theories is structure B.

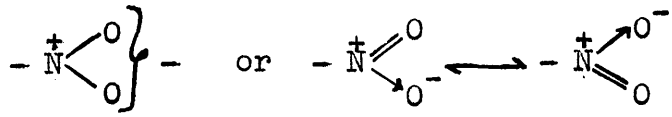
From a physical standpoint, the powerful influence of the nitro group may be attributed in the first place to the large nuclear charges of oxygen and nitrogen. This effect is reinforced, however, by the presence of a semi-polar bond which provides a permanent positive charge on the nitrogen atom. Williams (J.A.C.S. 1928,50,362) gives the dipole moments of nitrobenzene = 3.9, toluene = 0.4, o-nitrotoluene = 3.75, m-nitrotoluene = 4.2, and p-nitrotoluene = 4.5. Normally para dinitro compounds would be expected to be non polar or highly polar according to their structure e.g.



A. B - non polar C - highly polar.

Para dinitro compounds have no resultant dipole moment, indicating that the dipole moment of the nitro group is vectorially directed between the two oxygen atoms and not /

not at an angle as would be expected from the semi-polar bond formation, A. Williams (Phys.Zeit 1928,29,176 and 683), therefore maintains that, since it is impossible to differentiate in any way between the two oxygen atoms, the structure of the nitro group should be designated thus,



NITRIC ACID :

Spectroscopic investigations (Hantzsch, Ber. 1925,58,954) show that the alkali salts and esters of nitric acid have different absorption spectra in the ultra violet region of the spectrum. The spectrum of the concentrated acid is that of the esters while the spectrum of the dilute acid is identical with that of the alkali salts. Ordinary concentrated nitric acid is a mixture of the pseudo acid, nitronium nitrate and hydroxonium nitrate (fig. 1 structures D,M,L respectively). The equations connecting these compounds and the effect of dilution on pseudo acid is shown in fig.1.

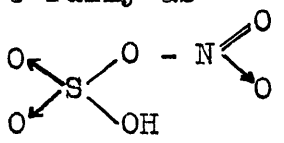
NITRO SULPHURIC ACID :

The existence of this acid together with its constitution is in doubt. It is formed according to the equation /

equation -

$$HO.NO_2 + H_2SO_4 = HO.SO_2.O.NO_2 + H_2O$$

The configuration usually given to this acid is shown in fig. 1 or more fully as



OXIDES OF NITROGEN :

Although nitrogen pentoxide and nitrous acid have complete outer electron shells, nitrogen peroxide (NO_2) possesses an odd number of electrons and therefore an incomplete shell. In this respect nitrogen peroxide resembles the free radicles. This resemblance probably accounts for its dimeric structure at low temperatures and for its strong additive properties.

NITROSYL SULPHURIC ACID :

Four possible structures (Mellor, Inorg.Chem. Vol.10, p.384) exist for this compound which was first noticed in the lead chamber process for the manufacture of sulphuric acid. In addition it may be formed as follows :

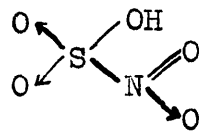
(1) $HNO_2 + H_2SO_4 = O_2S\begin{matrix}OH\\NO_2\end{matrix} + H_2O$

(2) $H_2SO_3 + HNO_3 = O_2S\begin{matrix}OH\\NO_2\end{matrix} + H_2O$

(3) /

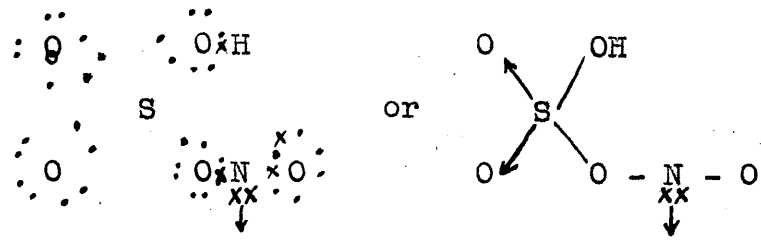
(3) $N_2O_4 + H_2SO_4 = O_2S(OH)(NO_2) + HNO_3$

Structure E, fig.1, assumed to be a stable complex, yellow in colour and showing the different types of linkages, may be represented thus :



In this structure, each element has a complete outer shell of electrons. The compound should, however, be capable of forming addition compounds since sulphur can exert a covalency maximum up to six.

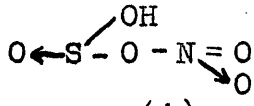
The compound, existing as colourless crystals, which in concentrated sulphuric acid solution partially reverts to structure E, as indicated by the yellow colour, is assumed to have the structure F. The structure may be represented thus :



showing the presence of a lone pair of electrons attached to nitrogen which would facilitate addition with a compound deficient in electrons or with one in which /

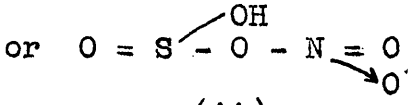
which one element is capable of exerting a higher covalency number. It is difficult, however, to associate this structure with nitration; nitrosation would be more probable.

The compound of structure G, by analogy with the structures for nitrating agents, is in all probability the nitrating form of nitrosyl sulphuric acid. It may be represented as



(i)

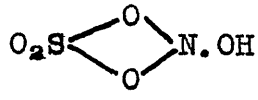
or



(ii)

(ii) showing complete saturation of electron shells, whereas (i) has a lone pair of electrons attached to sulphur which would account for the formation of addition compounds.

The fourth structure suggested is



which accounts for many of the reactions of nitrosyl sulphuric acid but does not account for its nitrating properties.

CHAPTER 3.

SUB SECTION A.

THEORIES OF NITRATION.

The following are the main theories of nitration, special stress being laid on the aldolization theory, though of late the cation theory has been gaining prominence.

(1) SIMPLE SUBSTITUTION :

A nuclear hydrogen atom reacts with pseudo nitric acid in the presence of a dehydrating agent or utilising the additive vapour pressures of an immiscible entrainer and of water formed during the nitration (Othmer, Jacobs and Levy, Ind.Eng.Chem. 1942, 34,286).

$$Ph.H + HO.NO_2 = Ph.NO_2 + H_2O$$

The objection to this suggestion is that it does not explain the varying percentage of isomers obtained by the nitration of the one compound using different nitrating acids.

(2) SULPHONATION :

The sulphonation theory was suggested by Cross, Bevan and Jenks (Ber. 1901,34,2496). The sulphonic acid group is first introduced into the aromatic nucleus, thus making the compound soluble in the /

the acid layer. Nitric acid then replaces the sulphonic acid group with a nitro group (cf. p. 75a)

$$PhOH + HO.SO_3H = C_6H_4(OH) - SO_3H + H_2O$$

$$C_6H_4(OH) - SO_3H + HO.NO_2 = C_6H_4(OH) - NO_2 + H_2SO_4$$

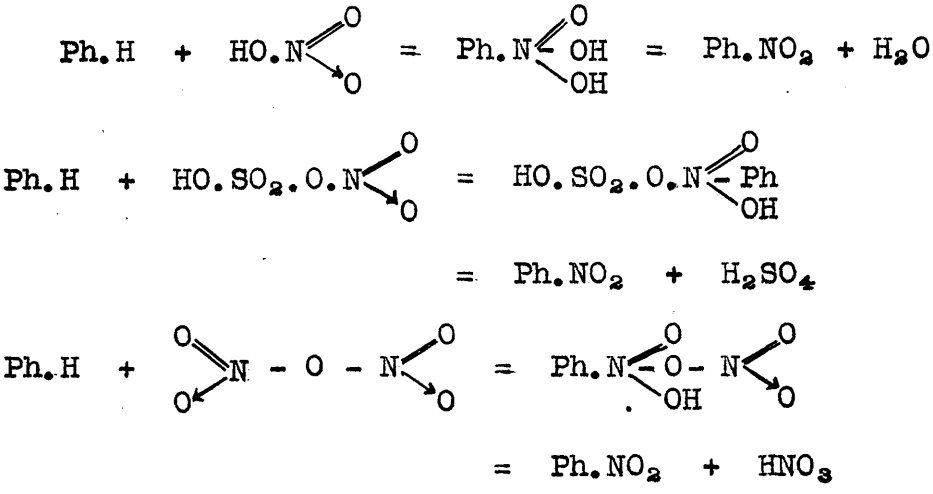
As an alternative to sulphonation preceding nitration, it is possible to have salt formation or even the formation of a loose addition compound between the hydrocarbon and the sulphuric acid, thus accounting for the peculiar behaviour of sulphuric acid in some cases, e.g. in the case of the nitration of aniline sulphate, the chief products are ortho and para nitraniline, but if the nitration is carried out in the presence of a large excess of sulphuric acid the meta isomer predominates (Nölting and Collin, Ber. 1884,17,261).

(3) ADDITION AND ELIMINATION : ALDOLIZATION THEORY.

The facts concerning the various nitrating mixtures agree more closely with this theory than with the preceding ones. Michael and Carlson (J.A.C.S. 1935,2,1268) have proved that the nitration of ethylene derivatives is indirect through the nitrous acid generated in oxidation side reactions; when it functions normally, unchanged nitric acid adds H and $O.NO_2$ /

$O.NO_2$ to the ethenic carbons.

For aromatic nitrations they suggested that nuclear hydrogen unites with a Δ (double bonded) oxygen of the acid, the residual aromatic group uniting with the nitrogen. Water is then eliminated to give the nitro compound e.g.



This aldolization process was suggested because a Δ oxygen of nitric acid must have a considerably higher content of free energy than the partially hydrogenised oxygen of the hydroxyl grouping, as well as a greater affinity for hydrogen. It can, therefore, more easily perform the work necessary to cause the hydrogen to migrate from the nuclear carbon. Thus, the dominating forces in nitric acid appear to be the chemical affinity of an oxygen for a hydrogen atom and that of a nitrogen atom for an aryl group.

(4) /

(4) CATION THEORY.

It has been suggested by Hetherington and Masson (J.C.S. 1933,105) that the nitrating agent in the nitration of mono to dinitro-benzene is the cation $C_6H_5.NO.OH^+$. More recently Usanovich and Cluchov (J. Gen.Chem.U.S.S.R. 10, No.3, 1940,227-9) have stated that nitration appears to be due to the nitrating cation $N.(OH)_3^+$ or $NO.(OH)_2^{++}$, Usanovich and Suskevich (ibid, p.230-2) from electrochemical evidence confirmed that viewpoint. These ions can however be rearranged to include pseudo nitric acid, and nitration may then proceed as in the case of the latter - the ionic structure promoting greater solubility in the acid, e.g.

$$H_3NO_3^{++} = HO.NO_2.2H^{++}$$

$$H_2NO_3^{+} = HO.NO_2.H^{+}$$

For discussions on the probable mechanism of nitration see Wieland and Sakallerios (Ber. 1920,53, 203), Wieland and Rand (Ber. 1921,54,1770) and Holleman - Die Direkte Einfuhrung Substituenten in den Bengolkern p. 476.

CHAPTER 3.

SUB SECTION B.

MECHANISM OF SOME NITRATIONS.

The mechanism of aliphatic nitration is probably fundamentally different from aromatic nitration, but it is only the latter with which this work is concerned.

It is possible by simple equations to show the reactants and products of a particular nitration, but the mechanism of the process is still doubtful. This may, in part, be due to the controversy over the structure of the benzene nucleus and to insufficient knowledge of the nature of the nitric acid molecule. The chief difficulty is the inability to specify the active nitrating agent. It may be pseudo nitric acid, nitronium nitrate, nitro sulphuric acid, nitrosyl sulphuric acid or the oxides of nitrogen. In fact, all are probably nitrating agents differing only in the ease with which they form "loose" addition compounds, e.g. the compound undergoing nitration may have a greater affinity for, say, pseudo nitric acid than for the oxides of nitrogen, so that in this case the nitric acid would be the true nitrating agent.

Lauer /

Lauer and Oda (J.Prakt.Chem. 1936,144,176, 146, 61) and Martinsen (Z.Phys.Chem. 1904,50,385; 1907,59, 605) found that the nitration of benzene derivatives in dilute homogeneous solutions in concentrated sulphuric acid follows a bimolecular reaction equation. The chemical mechanism of nitration most widely accepted is perhaps the addition - elimination theory but this mechanism is not based on kinetics and throws no light on it. Almost no work has been done on the physical mechanism of heterogeneous nitration although Hough and his collaborators (Chem. and Met.Eng. 1920, 23,666) have conceived it more or less as an interfacial reaction. Recently however, Lewis and Suen Ind.Eng.Chem. 1940,32,1095) investigated the heterogeneous nitration of benzene.

For the nitration of nitrobenzene, Hetherington and Masson (J.C.S. 1933,105) have suggested that it is the cation $(C_6H_5.NO_2.H)^+$ which is responsible for the nitration of the above compound. The promoting action of sulphuric acid and the inhibiting action of water and nitrobenzene is traced to the reversible hydration of the acid concerned and to competition between the nitrobenzene or water and sulphuric acid.

(1) /

(1) $H_2SO_4 + (H_3O)^+NO_3^- \longleftrightarrow (H_3O)^+ HSO_4^- + HO.NO_2$

(2) $H_2SO_4 + C_6H_5.NO_2 \longleftrightarrow (C_6H_5.NO_2.H)^+ HSO_4^-$

(3) $HNO_3 + C_6H_5.NO_2 \longleftrightarrow (C_6H_5.NO_2.H)^+ NO_3^-$

(4) $(C_6H_5.NO_2.H)^+ + H_2O \longleftrightarrow C_6H_5.NO_2 + H_3O^+$

(5) $(C_6H_5.NO_2.H)^+ + HNO_3 \longrightarrow C_6H_4.(NO_2)_2 + H_3O^+$

NITRO SULPHURIC ACID - fig. 1 (p. 9)

It has been suggested that the real nitrating agent in a sulphuric - nitric mixed acid is the mixed anhydride nitro sulphuric acid. As nitration progresses, sulphuric acid breaks off, forms hydrates thus diminishing its capacity for further dehydration.

$$HO.NO_2 + H_2SO_4 = HO.SO_2.O.NO_2 + H_2O$$

$$HO.SO_2.O.NO_2 + Ph.H = Ph.N(=O)(OH) - O.SO_2.OH$$

$$= Ph.NO_2 + H_2SO_4$$

$$H_2SO_4 + H_2O = H_2SO_4,H_2O$$

The similar preparation and successful employment of other analogous mixed anhydrides (e.g. acetyl nitrate) constitutes further evidence that nitro sulphuric acid is the active component in a mixed acid. On the other hand, the constitution of this acid is still uncertain, and its activity is generally attributed to its dehydrating properties. In support of the last statement is the fact that a solution of nitro sulphuric /

sulphuric acid will not nitrate benzene whereas a 46% solution in fuming nitric acid gives a good yield of nitrobenzene (Varma and Kulkarni, J.A.C.S. 1925,47,143).

OXIDES OF NITROGEN:

The function of the oxides of nitrogen is interesting and will provide ample basis for future research. In the nitration of alkanes by nitric acid oxidation occurs accompanied by the liberation of oxides of nitrogen, which appear to be essential: this has led to the belief that the nitrogen oxides are the true nitrating agents (Groggins, Unit processes in Org. Chem. p.3). In many cases their effect is merely catalytic, e.g. in the nitration of phenol (Kartashev, J.Russ.Phys.Chem.Soc. 1930,62,2129-2160) or toluene (p. 196). Catalytic effect of the oxides of nitrogen may be explained thus: (a) the compound undergoing nitration will have a greater affinity for the oxides of nitrogen than for the nitrating agent $HO.NO_2$. The formation of this additive compound will either weaken the bonds in the benzene ring, facilitating the entrance of the nitro group or weaken the bonds in the oxide of nitrogen facilitating its decomposition. (b) the inhibiting effect of these oxides (especially NO_2 p. 11) with its odd /

odd number of electrons) may be explained by assuming the formation of a stable addition complex, which tends to resist further addition in the benzene nucleus. (c) in the case where the oxides of nitrogen have no effect, the substance to be nitrated has a greater affinity for the nitrating agent than for the oxides of nitrogen.

Alternatively the formation of nitrosyl sulphuric acid, which then becomes the active nitrating agent, may explain the action of the oxides of nitrogen.

Nitrogen Pentoxide :

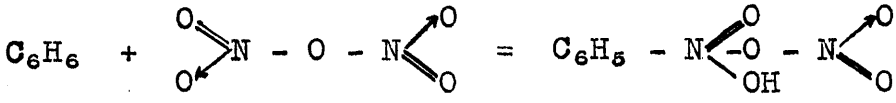
Klemenc (Monatsh. 1898,39,641) showed that N_2O_5 is formed as a result of the dehydrating action of concentrated sulphuric acid on nitric acid. From a study of mixed acids of 100% total acidity by the Raman effect, Chedin (Compt.Rend. 1936,202,1067) obtained the following :

HNO_3	10%	20%	40%	60%	80%
H_2SO_4	90%	80%	60%	40%	20%
N_2O_5	10%	12.5%	11.5%	10%	7.8%
$HO.NO_2$	0	7.5%	28.5%	50%	72.2%

When water is present in the mixed acid the percentage N_2O_5 is markedly diminished e.g. with 80% H_2SO_4, 10% HNO_3 /

HNO_3, 10% H_2O the amount of N_2O_5 is 3.4%. Nitration by this oxide may be explained by the following equations.

$$2HNO_3 + H_2SO_4 = N_2O_5 + H_2SO_4,H_2O$$



$$= C_6H_5.NO_2 + HO.NO_2$$

Nitrogen Peroxide :

N_2O_4 alone exhibits little reactivity with aromatic hydrocarbons, This behaviour is attributed to the slight tendency of NO_2 to add to benzenoid compounds, which do not contain an hydroxyl grouping. With increasing substitution in the benzene ring, the capacity of the aromatic compound to react with NO_2 increases. In presence of aluminium or stannic chlorides, benzene, toluene and chlorobenzene form stable addition compounds with NO_2 of the type

$$2\ Al.Cl_3.3(C_6H_5.CH_3.N_2O_4)$$

(Schaarschmidt, Z. angew. Chem. 1924, 39, 933). On hydrolysis, these hygroscopic metallic complexes are decomposed and yield a nitro compound and nitrous acid.

Naphthalene reacts smoothly with NO_2 in carbon tetrachloride solution, but is unreactive in ether solution. /

solution. This difference is due to the formation of an additive compound of ether with NO_2 which is no longer capable of addition to naphthalene (Schaarschmidt, loc.cit.). Phenols are readily nitrated by a benzene solution of N_2O_4 (U.S. 1933, 1917400)

Alternatively, NO_2 may act as a nitrating agent in sulphuric acid solution through the medium of nitric acid (Lunge, Ber. 1879,12,1058).

$$N_2O_4 + H_2SO_4 = HNO_3 + O_2S\begin{matrix}OH\\O.NO\end{matrix}$$

Nitrous Acid :

It is possible for this acid to act as a reducing agent in sulphuric acid solution. In addition to reduction, however, this acid can accelerate nitration reactions and is even a nitrating agent under certain conditions.

In the nitration of o- and p-phenol sulphonic acids the presence of nitrous acid is necessary to start the reaction. In no case was a nitroso derivative or a nitrite obtained (Veibel, Ber. 1930,63,1582). On the other hand, nitrous acid will nitrate dimethyl-p-toluidine, whereas nitric acid is inactive (Pinnow, Ber. 1895,28,3040) though mixed acid nitrated it (Morgan and Clayton, J.C.S. 1910,97,2645; cf Hodgson and Nicholson /

Nicholson, J.C.S. 1941,471).

Kartashev (J.Russ.Phys.Chem.Soc. 1930,62,2129) is of the opinion that the reaction of nitric acid on phenol is an auto catalytic process. Nitrous acid acts as a catalyst and its formation precedes that of the nitration product. The catalytic effect of nitrous acid may, in part, be due to the tendency to inhibit the formation of indophenol derivatives. It is emphasised that the nitrous acid is not an end product of the action of nitric acid upon phenol but enters into the process directly, being produced by the reduction of nitric acid by phenol and not by nitrophenols.

$$HNO_3 = HNO_2 + O$$

$$Ph.OH + HNO_2 = C_6H_4.N\begin{matrix}=O \\ H-OH\end{matrix} \text{ (which looses } H_2O\text{)}$$

$$C_6H_4.(NO)(OH) + HNO_3 = C_6H_4.(NO_2)(OH) + HNO_2$$

This indicates that nitroso phenol is an intermediate product in the reaction. In the nitrosation of phenol, however, the ortho and para compounds occur in different proportions to the final products obtained by nitration, thus casting doubt on the above mechanism.

CHAPTER 4.

FACTORS AFFECTING NITRATION.

In a nitration process, the choice of agent and the technique employed is governed by such factors as the chemical constitution, physical properties of the organic compound, and the cost of the process. The following are some of the more important factors to be borne in mind when considering a specific nitration.

(1) The nature and quantity of substance undergoing nitration.

(2) The composition and concentration of the nitrating acid.

(3) temperature.

(4) The time of contact.

(5) The speed of agitation.

(1) THE NATURE AND QUANTITY OF SUBSTANCE UNDERGOING NITRATION: The ease of nitration depends upon the nature of the group already attached to the aromatic nucleus. In general, it may be said that those groups, which direct the entering constituent into the ortho and para positions, facilitate the entry of nitro groups, although the halogens appear to have little effect on the rate of nitration. The meta directing substances, on the other hand, make nitration more /

more difficult. The influence of substituents in the benzene nucleus on the rate of nitration is as follows:

$$OH > OC_2H_5 > OCH_3 > Cl > COOH > SO_2OH > NO_2$$

POSITIVE NEUTRAL NEGATIVE

(Martinsen, Z.Phys.Chem. 1904,50,385-435; 1907,59,605-634 also Rice, Mechanism of Homogeneous Organic Reactions p.146)

Hetherington and Masson (J.C.S. 1933,105) have shown that in the nitration of mono- to di-nitrobenzene, excess of nitro compound extracts a large quantity of nitric acid together with some sulphuric acid and water from the mixed acid. This fact has been confirmed for the nitration of mono- to tri-nitrotoluene (p. 186). Thus, the formation of two phases reduces the rate of nitration.

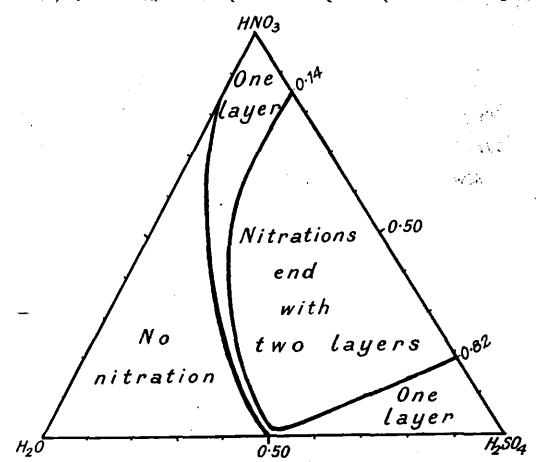
Furthermore, in the nitration of nitrobenzene, the addition of m-dinitrobenzene prior to the start of the reaction has little effect on the nitration unless only a small concentration of sulphuric acid is present, when it exhibits a slight inhibiting effect. Excess of nitrobenzene, however, affects the nitration in that the reaction proceeds more slowly and appears to cease at an early stage.

Moreover, they have shown that, when nitrobenzene /

when nitrobenzene is shaken with aqueous sulphuric acid containing no nitric acid, the nitrobenzene dissolves to a small extent but reduces the concentration of the acid by extracting or combining with anhydrous acid.

In heterogeneous nitration, Lewis and Suen Ind.Eng.Chem. 1940,32,1095) found that the rate of nitration is relatively insensitive to the composition of the organic phase i.e. to the percentage conversion of benzene to nitrobenzene so long as the conversion is not above 80 to 90%. In accordance with Hetherington and Masson they found that nitration reactions proceed in both phases, and that the rates of nitration in both phases were constant, that in the acid phase being several fold the rate in the organic phase.

(2) THE COMPOSITION AND CONCENTRATION OF THE NITRATING ACID: The composition of the nitrating acid has outstanding effects on both the rate and the extent of nitration. Hetherington and Masson (loc. cit.) have emphasised that nitration is a function solely of the acid phase. They maintain that nitration ceases at a stage determined by the relative proportions of the three inorganic constituents viz. nitric acid, sulphuric /



Relation between final state of nitration mixture and molecular composition of initial acid.

FIG. 2.

sulphuric acid and water (fig. 2). For this reason, it is probably better to discuss this item under various sub-headings.

(a) H_2SO_4

Sulphuric acid is more than a mere dehydrating agent. Primarily, its function is to remove the water formed chemically during the nitration to maintain a sufficient concentration of pseudo acid (P. 8) in the mixture. It also acts as a solvent, tending to give homogeneous solution thereby increasing the rate of nitration. Moreover it controls, to a large extent, the nitration (especially trinitrations) by making possible higher reaction temperatures without concurrent oxidation. Furthermore, it may assist in the formation of the oxides of nitrogen, which apparently play a major part in some nitrations. Finally, sulphonation may precede nitration, especially in the naphthalene, anthracene and phenol series, facilitating to a certain extent the entry of the nitro group. In the case of the toluene sulphonic acids, however, this is not the case (p. 77).

There is a limiting ratio of H_2SO_4/H_2O, dependent on the nature of the substance undergoing nitration, which must be exceeded if nitration is to take /

take place. Martinsen (Z.Phys.Chem. 1905,50,385; 1907, 59,605), in investigating the dynamics of nitration in sulphuric acid solution concluded that the strength of the sulphuric acid had a marked effect on the velocity of nitration, which reached a maximum for an acid of composition $H_2SO_4, 0.7H_2O$. Groggins (Aniline and its derivatives, p.72) mentions that nitration with mixed acid proceeds at a technically useful rate only when the ratio of the number of mols of H_2SO_4 to the sum of the number of mols of H_2O + HNO_3 exceeds a certain ratio which happens to be unity in the case of benzene. Since then, Hetherington and Masson (loc.cit.) have shown that, in the nitration of nitrobenzene, if at least sufficient sulphuric acid be present to form the monohydrate with the water formed chemically plus that initially present, all the nitric acid will be available for nitration. If less sulphuric acid be present, all the nitric acid is not used. If a large excess sulphuric acid be present, it is possible to reduce the velocity of nitration, presumably because nitronium sulphate is formed, thus reducing the concentration of pseudo nitric acid.

$$HO.NO_2 + 2\begin{matrix} HO \\ HO \end{matrix}\!\!>\!SO_2 = \left[N(OH)_3\right](SO_4H)_2$$

Hantzsch /

(Hantzsch, Ber. 1925,58,941 and Farmer, J.S.C.I. 1931, 50,75-78T). This last statement only applies to low temperature reactions (mononitrations) for at higher temperatures nitronium sulphate decomposes.

The kinetics can be studied only with relatively unreactive benzene derivatives which, in addition, are moderately soluble in strong sulphuric acid. Data are available for nitrobenzene, nitrobenzoic acid, benzene sulphonic acid and anthraquinone. In each case the rate passes through a maximum with increasing acid concentration. Martinsen (loc. cit.), Lauer and Oda (J.Prakt.Chem. 1936,144,176; 146,61) found that the rate of nitration of nitrobenzene is three times faster in 95% than in 100% H_2SO_4; with benzoic acid the rate for the same concentrations of acid is more than 28 times faster. In the continuous nitration of toluene to M.N.T. M^{c}Kinley and White (Trans.Amer.Inst.Chem.Eng. 1944,46,43) show that in the range 0 - 20 mole H_2SO_4 a change of 3 to 33 mole % H_2SO_4 at constant HNO_3 concentration will bring about a tenfold change in the rate of nitration.

(b) HNO_3.

Nitric acid is generally a poor nitrating agent, since its constitution changes due to dilution with the water formed in the nitration. To overcome this difficulty /

difficulty it would be necessary to employ a large excess of nitric acid. Under such circumstances polynitro derivatives may be formed and oxidation is probable. In the presence of dehydrating agents, most mononitrations can be carried out with the theoretical amount of nitric acid. Lewis and Suen (loc.cit.) in studying the heterogeneous nitration of benzene, M^{c}Kinley and White (loc.cit.) in the nitration of toluene found that over a wide range of acid composition a variation of only three or four mole per cent in the nitric acid content can make a tenfold variation in the rate of nitration.

The ratios HNO_3/H_2O and H_2SO_4/HNO_3 must be exceeded over the limiting values which vary from substance to substance, in order that nitration should proceed. As the latter ratio suggests, the nitrating potential of a mixed acid is controlled by varying the amount of H_2SO_4.

The acids, H_2SO_4 and HNO_3, when first mixed have relatively low heat capacity (Ind.Eng.Chem. 1938, 30, 648), and very efficient stirring is necessary to control the temperature during the initial stages of nitration. On the other hand, "cycle acid" i.e. a spent acid, has a higher heat capacity when fortified with HNO_3 than the above acids and for this reason as well as for economy, it is often incorporated with the pure acid, temperature control being therefore

less /

less difficult . It is claimed that, by dissolving 3% boric acid in nitric acid, cooling is rendered unnecessary when sulphuric acid is added. The presence of boric acid, moreover, results in the sulphuric acid combining with the water formed during the nitration much more quickly and without the development of heat (Colver, High Explosives, p. 133).

If sulphuric acid be replaced by another dehydrating agent (e.g. by acetic anhydride) or, if the nitrating medium be changed (p. 24) the proportion of the various isomers present is usually altered. In this respect, it is worthy of note that, in the nitration of acyl or alkyl derivatives of aromatic amino compounds in the presence of concentrated sulphuric acid, the nitro group tends to enter the meta position with respect to the amino group and not the expected ortho or para position (J.C.S. 1922,121,526; 1926,1655 and 2440 also Ber. 1909,42,4151; cf. p. 10).

Different products may also be obtained according to the method of adding the reactants. For example, when toluene is added to an acid of composition, one part HNO_3 (sp.g. 1.42) to two parts H_2SO_4 (sp.g. 1.84), the product consists of 60% mono and 40% dinitrotoluenes.

On /

On the other hand, if the acid is added to the toluene, very little dinitro compound is formed although the temperature is more difficult to control. Hoffman, Met. and Chem. Eng. 8,998 also Escales, Nitrosprengsstoffe 1915,6,133).

(c) Oxides of Nitrogen.

A sulphuric - nitric mixed acid usually contains oxides of nitrogen either in solution or in combination. Generally, oxidation occurs at the expense of nitration when these oxides are present but as has been stated (p. 21) they (especially HNO_2) often exert a catalytic effect. The acid (HNO_3) may be freed from these oxides by air blowing or in small scale nitrations by the addition of urea or amino sulphonic acid.

(3) TEMPERATURE: The purity of the product is governed to a large extent by the temperature at which the nitration is carried out. In general, the temperature should be as low as possible to avoid oxidation, but this factor must be considered in conjunction with the time factor, i.e. at low temperatures, longer time is required for complete nitration. On the other hand, within limits, the higher the temperature the more nitro groups are introduced and in a trinitration process, /

process, for example, a compromise must be made between these two extremes. Martinsen in homogeneous medium and Lewis and Suen in heterogeneous media found that a 10°C rise in the temperature of nitration resulted in a two to three-fold increase in the rate of nitration.

Temperature also affects slightly the proportion of the various isomers formed. In the nitration of toluene, rise in temperature results in a slight increase in the meta isomer while the para is decreased by a corresponding amount. The following table is due to Holleman, Proc. K. Akad. Wetensch, Amsterdam, 1908,11,248).

Temp.	% ortho M.N.T.	% meta M.N.T.	% para M.N.T.
- 30°C	55.6	2.7	41.7
0°C	56.0	3.1	40.9
30°C	56.9	3.2	39.9
60°C	57.5	4.0	38.5

On the other hand, in the nitration of mono to dinitrobenzene, increase in temperature lowers the relative yield of meta compound. The following table, due to Pounder and Masson (J.C.S. 1934,1352) illustrates the point with reference to the nitration of mono to dinitro - benzene.

Temp. °C /

Temp. °C	% meta(m)	% ortho(o)	% para(p)	$\frac{m}{o+p}$	$\frac{o}{p}$
0	93.70	5.8	0.55	14.90	12.0
35	90.15	8.1	1.75	9.15	4.6
60	87.30	11.5	1.20	6.90	9.6

The temperature of nitration is determined by the number of nitro groups to be introduced and can generally be controlled by the amount and concentration of the sulphuric acid to be used.

(4) THE TIME OF CONTACT: The time of contact, taken in conjunction with the acid composition, and, to a lesser extent the temperature, governs the quality of the product and the degree of nitration. The longer the time of contact between the fully nitrated substance and the acid, the greater is the chance of oxidation, which in turn usually affects the colour of the nitrobody - an important industrial consideration. Moreover, nitrobodies, especially polynitro compounds, tend to become unstable if kept for long times in contact with acid.

(5) SPEED OF AGITATION: Nitration being an exothermic reaction due to the heat of formation of nitro compounds and to the heat of dilution of the sulphuric acid usually present, agitation must be very efficient to distribute the heat rapidly and evenly. For substances, which form heterogeneous mixtures with the nitrating acid, efficient stirring is specially important, because on it depends the rate of reaction (p.192).

CHAPTER 5.

NITRATION PRODUCTS OF TOLUENE.

(a) PROPERTIES.

The physical and chemical properties of the nitrotoluenes may be obtained from such standard text books as: Colver, High Explosives; Marshall, Explosives; Smith, Nitrotoluenes. In addition ber. 1906,37,1256; 1914,47,1718; J.S.C.I. 1908,27,258 also J.C.S. 1922, 121,270 may be consulted.

The following main characteristics are listed for convenience. (cf. Beil. V pp. 318,322,323).

Substance	Sp. G.	M.P. °C	B.P. °C	Ref. Index.
Toluene	D_4^{15} 0.869		110.10	n_D^{20} 1.54739
o-Nitrotoluene	D_4^{15} 1.168	-10.56(α) - 4.14(β)	222.3	n_D^{21} 1.54620
m-Nitrotoluene	D_4^{22} 1.168	+ 16	230	n_D^{21} 1.5470
p-Nitrotoluene	D_4^{54} 1.123	+51.6	237	

Omstromisslensky (Z.Phys.Chem. 1907,57,341) states that in the solid state o-nitrotoluene exists in two forms. The alpha modification is meta stable and in the literature has a melting point ranging from -8.95 to -10.56°C. The beta form is stable and in the literature melting points ranging from -3.6 to -4.25°C are quoted. On cooling o-nitrotoluene, the alpha form is first /

first obtained. This, however, quickly changes to the beta modification, with the liberation of heat. The beta form can also be obtained by seeding the supercooled liquid with beta crystals or by cooling the liquid to -50 to -60°C. The beta form can be transformed into the alpha form by heating to 50°C then cooling or by inoculating the supercooled liquid with alpha crystals.

The M.N.Ts. differ from D.N.T. and T.N.T. in forming addition products with inorganic salts which are generally unstable e.g. $AlCl_3.C_6H_4(CH_3)(NO_2)$, (C.1910,1, 164,1240; 1913,1,805).

DINITROTOLUENES.

Substance	designated	m.p. °C
2:4- D.N.T.	alpha	70
2:6 "	epsilon	66
3:4 "	zeta	60, 58.5, 61.
2:3 "	gamma	63, 59.23
2:5 "	delta	48, 50.25, 52.5.
3:5 "	beta	92- 93

Alpha - monoclinic, yellow needles, insoluble in water, soluble in alcohol, ether, carbon bisulphide, benzene.

Beta - yellow needles on crystallising from a mixture of acetic acid and benzol.

Gamma - Hair-like needles when crystallised from dilute acetic acid.

Delta /

Delta - yellow needles from ligroin.

Epsilon - yellow needles from alcohol.

Zeta - very long needles when crystallised from carbon bisulphide.

The chemical properties of the D.N.Ts. have not been studied so closely as those of the M.N.Ts or T.N.Ts. They form additive compounds like T.N.T. especially with M.N.T. and T.N.T. The resulting additive compounds melt some 30 to 40°C lower than the initial melting point of the D.N.T. (Will, Ber. 1914, 47,1718).

TRINITROTOLUENE.

Substance	designated	m.p. °C
2:4:6	alpha	80.85
2:3:4	beta	112
2:4:5	gamma	104
3:4:5	delta	137.5
2:3:5	epsilon	97.2
2:3:6	zeta	79.5

The solubilities of alpha, beta and gamma T.N.Ts. are practically identical. All three isomers are very slightly soluble in cold water, slightly soluble in cold alcohol and very soluble in ether, acetone, ligroin, hot glacial acetic acid. Alpha T.N.T. is very soluble in hot /

hot alcohol whereas beta and gamma T.N.Ts. are only moderately soluble and this fact is made use of in the separation of alpha from beta and gamma T.N.Ts. Hot glacial acetic acid may be used to break up partially the beta-gamma T.N.T. eutectic, m.pt. 80°C, but the best method is to dissolve the eutectic in concentrated H_2SO_4 heated to 110°C; on cooling, the beta isomer crystallises first. The following solubilities for alpha may be given:

Water at 15°C 0.021% 100% H_2SO_4 at 15°C 6.6%
Alcohol at 15° 1.6% " " " 100°C very soluble.
Alcohol at 78° 10.0%

(see also J.A.C.S. 1923,45,58)

The action of dimethyl aniline or aniline divides alpha, beta and gamma T.N.T. into two classes

(a) the alpha form constitutes the first class in which one molecule T.N.T. forms an addition compound with one molecule aniline.

(b) the beta and gamma isomers constitute the second class in which one molecule T.N.T. reacts with three molecules of the base, forming decomposition instead of additive compounds

$C_6H_2(CH_3)(NO_2)_3 + 3PhNH_2 = PhN_2NHPh + C_6H_2(CH_3)(NO_2)_2NHPh$

Alpha, beta and gamma T.N.Ts react with naphthalene in benzene /

benzene solution to form yellow needle shaped crystals, m.pt. 97-98, 100 and 88-89°C, respectively. Anthracene and also alpha and beta naphthylamine behave similarly.

The three isomeric T.N.Ts. can further be distinguished by the action of caustic alkali. Two molecules of alpha T.N.T. may react with one molecule alkali thus:

$2\ C_6H_2(CH_3)(NO_2)_3 + NaOH = (NO_2)_3C_6H_2\text{-}CH_2C_6H_2(NO_2)_3.$

Beta and gamma T.N.Ts., on the other hand, react with one molecule alkali to form dinitro cresols.

In all these reactions the nitro group that is meta to another nitro group and ortho or para to the methyl group does not react (p. 46). In the majority of chemical reactions gamma T.N.T. reacts more quickly than beta T.N.T.

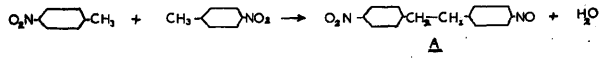
(B) THE ACTION OF ALKALI ON THE NITROTOLUENES.

MONO NITRO TOLUENE.

Pure ortho, meta and para M.N.T. react slowly with cold aqueous alkali.

Perkin (J.C.S. 1880,37,546), by the action of alcoholic caustic potash on para M.N.T., obtained a red insoluble product. Klinger (Ber. 1883,16,943) and later Bender and Schultz (Ber. 1886,19,3234) found that this substance on complete reduction gave a diamino stilbene and /

ALKALI ON PARA M.N.T.
SUGGESTED MECHANISM



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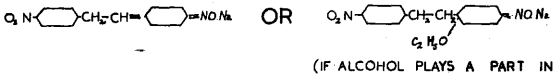
THE RED SODIUM SALT HAS THE FOLLOWING STRUCTURE



(IF ALCOHOL PLAYS A PART IN THE REACTION.)

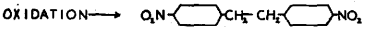


FIG. 3.

and as a result the two latter authors considered Perkin's product to be an azoxy stilbene $(C_7H_5)_2N_2O$.

Fischer and Hepp (Ber. 1895,28,2281) repeated Perkin's preparation and found it corresponded to dinitroso stilbene. Green and collaborators (J.C.S. 1904, 85,1424 and 1432; 1906,89,1602; 1907,91,2076) investigated the above compound and found that by gently warming a mixture of 33% methyl alcoholic potash with para M.N.T. a blood red colouration was developed. This on vigorous shaking with air gradually faded and by continuing the process a yellow crystalline deposit was obtained in the liquid of 4:4'-dinitro-dibenzyl. The mechanism suggested was according to figure 3. Generally, the action of methyl alcoholic potash on a nitrobody is to produce the azoxy compound.

By altering the conditions slightly it is possible to obtain 4:4'-dinitro stilbene or 4:4'-dinitroso stilbene which condenses to dinitro-azo-distilbene.

Ortho M.N.T. may be freed from the para isomer (J.S.C.I. 1888,7,593 also Ch.Z. 1888,12,787) by cohobating for 24 hrs. 100 gms. commercial ortho M.N.T. with 25 gms. NaOH, 25 gms. H_2O, 50 gms. C_2H_5OH then diluting with water, acidifying slightly and distilling with steam. The para isomer is more readily attacked by alcoholic /

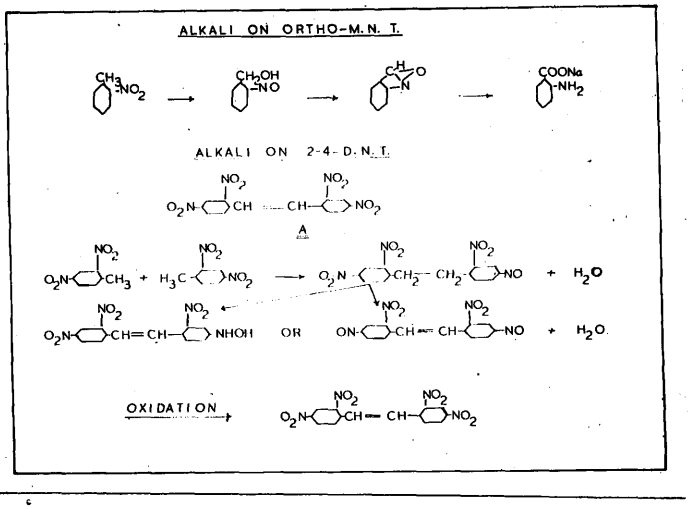


FIG. 4.

alcoholic caustic soda according to the above equations, than is ortho M.N.T. Ortho M.N.T., on treatment with NaOH undergoes the following series of reactions (fig.4). It is possible to remove ortho and para M.N.T. from meta M.N.T. by means of their reaction with ethyl oxalate + sodium ethoxide. On the completion of the reaction the mixture is acidified and steam distilled when meta M.N.T. passes over.

DINITROTOLUENE.

Alcoholic caustic potash on 2:4-D.N.T. under conditions akin to that of para M.N.T. gives a deep blue colour but air oxidation in this case is not effective and consequently no identifiable product can be isolated. If, however, the reaction is carried out in pyridine -methyl alcoholic solution in the presence of iodine as an oxidising agent 2:4-2':4' tetranitrostilbene is obtained (fig.4, structure A). The mechanism suggested was as in fig. 4.

ALCOHOLIC ALKALI ON T.N.T.

De Bruyn and Van Leent (R. 1895,14,150) obtained red crystals of a compound $C_6H_3(NO_2)_3.CH_3OK,\frac{1}{2}H_2O$ by the addition of potassium methylate to a solution of trinitrobenzene in methyl alcohol. T.N.T. gives a dark red crystalline precipitate which on washing with alcohol and benzene, followed by drying at room temperature inflames/

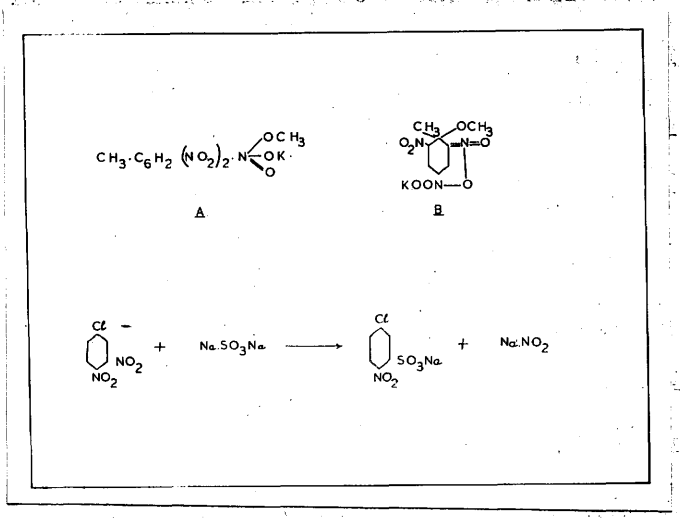


FIG. 5.

inflames at 130 to 150°C and occasionally explodes. The salt is readily soluble in water and gives precipitates with solutions of salts of various metals e.g. the one with copper tetraminonitrate is a brick red powder detonating violently at 120°C. Sodium salts can also be obtained.

Hantzsch and Kissel (Ber. 1889,32,3137) regarded the salt of T.N.T. formed by the action of methyl alcoholic caustic potash as in fig.5 structure A which shows T.N.T. functioning as a pseudo acid. The above compound on acidification gave a red amorphous body which they regarded as the free acid, though Hantzsch subsequently realised that it was in reality a complex decomposition product.

Hantzsch and Picton (Ber. 1909,42,2119), from work on the action of potassium methylate on trinitro phenetole, represent the structure of the coloured salt of T.N.T. as in fig.5 structure B.

Beta and gamma T.N.Ts. give phenolic bodies as tars. 3:4:5-T.N.T. gives 3:5-dinitro-p-cresol m.pt.81.5 °C, 2:3:6-T.N.T. gives a dark brown precipitate.

Moreover, by the substitution of ethyl or propyl alcohols for methyl alcohol the corresponding salts are obtained. In the case of propyl alcohol, hoever, the salt is difficult to obtain pure due to oxidation /

oxidation side reactions. The latter salt is red in colour and detonates at 50 to 60°C and sometimes even at room temperature (Ber. 1910,43,1564).

On acidifying aqueous solutions of one of these salts a brown amorphous body is precipitated which is insoluble in cold benzene but is readily soluble in acetone. On heating, this amorphous body does not detonate but deflagrates slightly leaving a voluminous mass of carbon.

The addition of alcoholic caustic potash to an acetone solution of gamma T.N.T. gives a violet colour turning grey: an acetone solution of beta T.N.T. gives an intense violet colour: an acetone solution of delta T.N.T. gives a pale rose colour. A solution in acetone treated with one quarter of its volume of 95% ethyl alcohol and one drop of alcoholic caustic soda gives a blue violet colour with gamma; an intense green colour turning to crimson with beta (cf. Ind.Eng.Chem.(Anal.), 1935,7,190).

AQUEOUS ALKALI ON T.N.T.

Secondary reactions in aqueous alkali take place more readily than in alcoholic solution with the result that it is difficult to isolate pure compounds. The T.N.Ts. react only slowly in the cold, unlike the action /

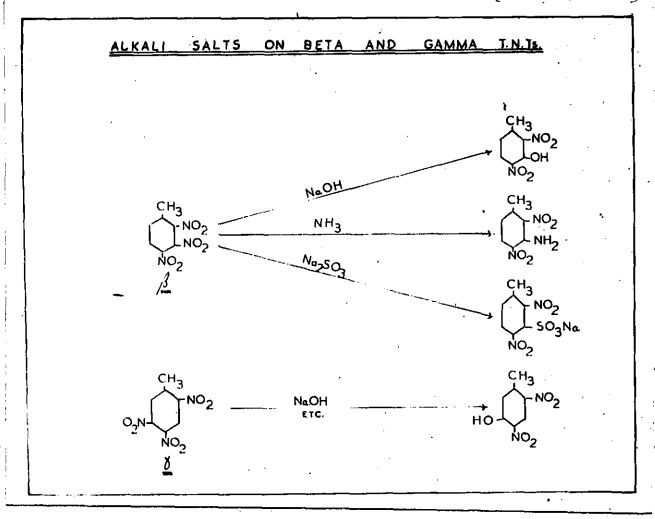


FIG. 6.

action with alcoholic alkalis, but do so more readily at 50°C to give the same type of compounds as above e.g. with T.N.T. a compound m.pt. 212°C and which is probably hexanitrodibenzyl is obtained (Mécir, Chim.et Ind. 1933, 29, Spec. No. p.952).

There is a distinct difference between alpha, beta and gamma T.N.Ts. in their reactions towards alkalis e.g. 2 mols alpha T.N.T. + 1 mol NaOH gives an unstable condensation product. Beta and gamma T.N.Ts., on the other hand, react in the ratio of 1:1 forming a derivative of cresols (fig. 6).

On heating T.N.T. with more concentrated alkali (30%) decomposition takes place with the evolution of ammonia. On acidifying the resulting solution, a black amorphous powder which does not deflagrate on heating and only slowly burns away when kept in the flame, is obtained.

AMMONIA ON BETA AND GAMMA T.N.Ts.

Ammonia on beta T.N.T. produces an olive green colouration turning red, which on gently heating changes to a greyish yellow. On cooling, a dinitro toluidine separates m.pt. 94°C. Ammonia on gamma T.N.T. gives a blue colouration which on heating turns brown and on cooling gives a dinitro toluidine m.pt. 192-3°C. 2:3:5-T.N.T. in acetone solution with ammonia gives a rose /

rose colour turning brown and finally black. The reactions are expressed in fig. 6.

The above facts are extracted from the following papers: Hepp, A. 1882,215,317; Will, Ber. 1914, 47,710; Brady, J.C.S. 1924,2,2400; Körner and Contardi, C. 1916,1,1019.

In addition, T.N.T., in the presence of traces of alkalis or of strong organic bases, is very reactive, combining readily with aldehydes or other organic bodies with evolution of much heat (p. 144).

Moreover, different products are obtained on acidifying alkaline solutions of T.N.T., illustrating the effect of pH.

(1) Extraction of solution with benzene gives a body melting with decomposition above 230°C.

(11) In methyl alcohol solution a compound, m.pt. 132°C results.

(111) In lime water solution a compound, m.pt. 135 to 184°C results.

(C) YIELDS ON NITRATION.

Previous work on the nitration of toluene is discussed by Hoffman (Tech. Paper 146, U.S. Bureau of Mines 1916). Rosenstiehl (A.Chim.Phys. 1872,27,433) states that toluene with HNO_3 (Sp.G. 1.42) is not nitrated /

Table 1.

Nitration of	Composition at		
	M.N.T. stage.	D.N.T. stage.	T.N.T. atage.
Toluene.	62.0% ortho 33.5% para 4.5% meta	74.8% 2:4 20.7% 2:6 2.5% 3:4 1.1% 2:3 0.9% 2:5	95.5% 2:4:6 2.9% 3:4:6 or 2:3:5 1.3% 2:3:4 0.3% 2:3:6
Para M.N.T.		100.0% 2:4	100.0% 2:4:6
Ortho M.N.T.		66.6% 2:4 33.4% 2:6	100.0% 2:4:6
Meta M.N.T.		Mixture of 3:4, 2:3 and 2:5.	63.1% 2:4:5 30.3% 2:3:4 6.6% 2:3:6
3:4 D.N.T.			90.0% 2:4:5 10% 2:3:4
2:3 D.N.T.			84.0% 2:3:4 16.0% 2:3:6
2:5 D.N.T.			87.0% 2:4:5 13.0% 2:3:6
3:5 D.N.T.			42.0% 2:3:5 8.0% 3:4:5 50% loss by oxidation.

Under the nitrating conditions used above the following D.N.Ts., 2:3, 2:5, 3:5 are not nitrated beyond 22%, 23%, and 7.3% respectively.

nitrated in the cold but with acid of Sp.G. 1.5 the following yields are obtained.

5 parts HNO_3(S.G. 1.5) at 40°C gives 64.8% p-M.N.T.

1 part " " " 40°C gives 43.5% p-M.N.T.

1 " " " -10°C gives 33.4% p-M.N.T.

Noelting and Forel (Ber. 1885,18,2672) showed that toluol with HNO_3 alone gives mainly p-M.N.T. (66%), whereas with sulphuric - nitric mixed acid mainly o-nitrotoluene (60 to 66%) is obtained.

Van der Arend (Verslagen Kon Akad. Wetensch, Amsterdam, 1908,11,206) carried out nitrations using excess of nitric acid and no sulphuric acid over a wide range of temperature (-30 to +60°C). He concluded from his results that temperature had little effect on the relative proportion of isomers, which was confirmed by Holleman (p.35). Gibson and collaborators (J.C.S. 1922, 121,270) confirmed the above figures using mixed acid.

Pictet (Ber. 1907,40,1163) by the action of acetyl nitrate in acetic anhydride solution on toluene, obtained a nitrotoluene of composition 88% ortho, 12% para.

Gibson and collaborators (loc.cit.) give the following yields for the nitration of toluene to the T.N.T. stage using mixed acid (table 1).

(D) METHODS /

(D) METHODS OF ESTIMATION.

(1) the percentage of toluene in M.N.T. may be determined by refractive index or by specific gravity.

(2) the percentage of D.N.T. in M.N.T. may be determined by specific gravity or refractive index.

(3) the percentage of D.N.T. in T.N.T. may be determined by specific gravity or dry set point determination.

(4) the estimation of ortho, meta and para nitrotoluene may be done thus:

(a) oxidation of the mixture of nitrotoluenes to the corresponding benzoic acids and analysis of these by determining the solubility in a solution saturated with respect to two isomerides (Ingold, J.C.S. 1931,1959).

(b) Hoffman (Ind.Org.Chem. 1,616) estimated the proportion by conversion to the toluidines and then to the oxalates. Ortho toluidine under the conditions of the experiment gives no oxalate while meta toluidine is precipitated as the normal oxalate, and the para isomer as the acid oxalate. The two latter are estimated by titration with NaOH (cf. Ber. 1903,36,4260).

(c) Gibson and collaborators (loc.cit.) used the method of thermal analysis.

(d) /

(d) the meta nitrotoluene content may be compared with that of a M.N.T. of fixed composition by nitrating under standard conditions and finally, after washing, determining the dry set point (cf. p. 81, 158).

(E) SEPARATION.

Fractional distillation in vacuum of nitro toluene can give pure ortho and para nitro toluene (Schön, Ch.Z. 1897,21,791; also Beilstein and Kuhlberg, A. 1870, 155,7). Strong cooling results in the separation of impure para nitrotoluene (Knoevenagel, Ber. 1909,42,512). Ortho nitrotoluene can be separated from small amounts of para nitrotoluene by boiling four parts of the mixture with one part caustic soda, one part water and two parts alcohol for twenty four hours, acidifying and distilling the ortho isomer in steam (Reverdin de la Harpe, Ch.Z. 1888,12,787). Another method is dependent on the sulphonation of crude nitrotoluene whereby the ortho nitrotoluene is sulphonated and para nitrotoluene remains unchanged (B.P. 1890, 1,407). It is also possible to separate the ortho isomer from the meta and para by submitting the mixture to the action of alkali arsenite and subsequently removing the reduction products leaving the ortho isomer which resists reduction (G.P. 1894;78,002).

The /

The above fact that para nitrotoluene is reduced more easily than the ortho isomer is the basis of a number of separations e.g. G.P. 1896, 92,991 describes the separation by the fractional reduction using alkali sulphides.

CHAPTER 6.

THE PURIFICATION OF T.N.T. BY SULPHITE.

Sodium sulphite, in the cold, attacks the unsymmetrical T.N.Ts. especially gamma with little loss of alpha T.N.T. It does not, however, affect D.N.T. chemically. If salts that are more or less distinctly alkaline are used, they tend to darken the T.N.T. and render it unstable; the loss of alpha T.N.T. is furthermore higher the greater the alkalinity. The alkaline solution is therefore adjusted to an initial pH of 7 to 8.3 by the addition of a weakly acid substance like boric acid or sodium acetate + acetic acid (I.C.I. and Davies, B.P. 1936,382,322).

Mécir (Chim. et Ind. 1933,29,Spec.No. p. 952) states that the longer the time of contact, the higher the temperature and the more concentrated the sulphite solution, the greater is the action on, and consequently the loss of, alpha T.N.T. Furthermore, the action of sulphite on unsymmetrical D.N.Ts. in the cold is very slight but at temperatures greater than 50°C they react. 2:4-D.N.T., on the other hand, does not react to any great extent even at elevated temperatures though some reaction takes place above 70°C. In addition, he states that the amount of sulphite required to eliminate the unsymmetrical T.N.Ts. in the cold, was twice the theoretical /

theoretical amount and that the sulphite concentration must not fall below 1%.

MECHANISM OF SULPHITING.

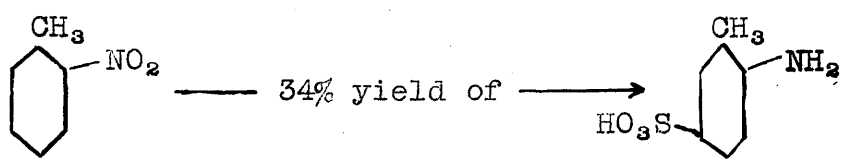
It is a general characteristic of ortho dinitro derivatives that one nitro group is labile and may be replaced by other groups. Laubenheimer (Ber. 1882,15, 597) showed that the action of sodium sulphite on 1-chloro-3:4-dinitrobenzene was as in fig.6. Similarly, Hepp (A. 188,215,344) showed that 2:3:4-T.N.T. gave 3-methyl-2:6-dinitrodiphenylamine while 3:4:6-T.N.T. gave 3-methyl-4:6-dinitrodiphenylamine with aniline. With ammonia 2:3:4-T.N.T. gave 3-methyl-2:6-dinitro aniline.

In support of the mechanism postulated by Laubenheimer, Brady and collaborators (J.C.S. 1924,125, 2400) isolated dinitrotoluene sulphonates from sulphite reaction with 3:4:5, 2:3:4 and 2:3:5 T.N.Ts. in the cold. Gornall and Robinson (J.C.S. 1926,1981) showed that 2:3:4-T.N.T. gave 2:4-dinitrotoluene-3-sulphonate. Muraour (Bull.Soc.Chim. 1924,35,367) confirmed Brady's work using dilute (3 to 5%) sulphite solutions on beta and gamma T.N.Ts. to give colourless solutions of the corresponding dinitrotoluene sulphonates as in fig. 6.

In addition, Muraour mentioned that the red colour produced when T.N.T. reacts with sulphite was due /

due to the formation of an addition product which is only stable in concentrated solutions of sulphite. At elevated temperatures Mécir (Chim. et Ind. 1933,29, Spec.No. p. 952) found that a brown amorphous powder is deposited melting with decomposition above 250°C which he concluded to be hexanitrodibenzyl. Batik, (Chim. et Ind. 1933,29, Spec. No. p. 960) on the other hand described a product isolated after acidification of spent sulphite and which appeared to be a nitrodiazo - -toluene sulphonic acid.

The Piria reaction (A. 1851,78,31) involves treatment with hot aqueous bisulphite followed by heating with mineral acid. During the reduction period (using $NaHSO_3$) it is known that the nitro group is transformed into an amino group, a sulphonic group or both



Hunter and Sprung (J.A.C.S. 1931,1,1432) state that the presence in the nucleus of a methyl group favours the formation of amines; of a carboxyl group or a second nitro group or a condensed ring, the formation of amino sulphonic acids. Moreover, they found that the speed of reduction increased with dilution and that neutral /

neutral sodium sulphite was able to reduce dinitro benzene in two hours whereas bisulphite required over eight hours, suggesting that the concentration of sulphite ions was important. On the other hand, they found that partially neutralised bisulphite was a more effective reducing agent than normal sodium sulphite.

There is no doubt that the reaction between cold sulphite and unsymmetrical T.N.Ts results predominantly in the formation of dinitrotoluene sulphonates. That other reactions are possible on the lines of the Piria reaction is indicated by (i) the production of coloured solutions by the action of sulphite on nitrobodies e.g. the deep red solution with alpha T.N.T., the orange-red solution with beta T.N.T. (ii) the excess of sulphite required in practice over theory.

The Piria reaction would explain (i) - the production of coloured solutions - through the formation of amines which may react with HNO_2 (since T.N.T. has a pH on the acid side) then couple to give azo compounds. The further interaction between excess sulphite and nitrite, produced according to equation in fig. 5, along lines suggested by Divers and Hagga (J.C.S. 1900,77,673; 1901,79,1093) and Andrieth (J.A.C.S. 1936,60,1947) may explain (ii) cf. also Chem. Reviews, /

Reviews, 1940,26,49.

The literature on the whole is vague with regard to hot sulphiting especially on the following points at varying pH values between 7 and 10.

(a) loss of alpha T.N.T.

(b) removal of D.N.T.

(c) the usage of sulphite (i.e. excess over theoretical) indicating side reactions which may involve reduction or interaction between sulphite and nitrite.

(d) the mechanism of the sulphite reaction with regard to alpha T.N.T. which behaves in a different manner to the unsymmetrical T.N.Ts.

E X P E R I M E N T A L

S E C T I O N.

Part 1.

GASEOUS AND ACIDIC BY-PRODUCTS.

SUB - SECTION A

GASEOUS OXIDATION LOSSES.

CHAPTER 7.

OXIDATION LOSSES IN MONONITRATION.

Oxidation represents one of the major losses in nitration especially when the substance undergoing nitration is to be fully nitrated. The loss can be clarified under two main headings (a) gaseous and (b) solid and it is the former that we are concerned with in this section.

In the nitration of toluene there are three well defined stages (a) toluene - M.N.T. (b) M.N.T. - D.N.T. and (c) D.N.T. - T.N.T. With regard to (a) the optimum temperature of nitration has long been a controversial point. Increase in temperature will increase the rate of nitration but the extent of the oxidation loss is not known.

The apparatus used was as in fig. 7, cf. p. 64 , with the addition of a tap funnel dipping under the surface of the mixed acid for introducing the toluene. The scrubbing bottles for the effluent gases contained dilute $KMnO_4$ solution to remove nitrous fumes. Gas analysis was conducted on the Haldane apparatus.

To simulate commercial mixed acid, an acid of composition 5% HNO_3, 3.8% HNO_2, 69.5% H_2SO_4, 21.7% H_2O was made up, half the theoretical amount of water being /

being added to the sulphuric acid and half to the nitric acid as ice. Both solutions were cooled in ice and the nitrogen peroxide added to the sulphuric acid by means of a tap funnel dipping under the surface. Finally the solutions were mixed and bottled. Putting conditions at their worst a 20% excess of HNO_3 was used, 358 gms. of the above mixed acid being added to the reaction flask and 25 ml. toluene pipetted into the tap funnel. The toluene used was a purchased sample of S-free grade having the following values for specific gravity and refractive index, $0.8713^{15.5}_{4}$ and 1.4969 at 20°C respectively.

The cooling water surrounding the reaction flask was adjusted to about 10°C below the desired temperature - as was also that of the contents of the flask. The pressure in the reaction flask was slightly reduced by allowing 2 to 3 bubbles of air per minute to enter the evacuated gas collector. The toluene was added in small amounts while the temperature, which quickly rose within the flask, was kept at the required figure to within $\pm$ 1°C by replacement of cooling water and addition of toluene alternately. The whole of the toluene was added in 5 to 10 minutes in each test - the duration of the test being one and a half hours from the time of the first addition of toluene. Stirring was maintained /

maintained throughout using a constant speed motor. For the first 85 mins. of running, only a very small amount of air was allowed to enter the gas collector but during the last 5 mins., the stream was increased so as to sweep into the collector all the gaseous products and bring the former to atmospheric pressure. After the temperature and pressure were noted a gas sampling tube was filled from the collector and attached to the Haldane for gas analysis.

Table 2. GASEOUS LOSSES EXPRESSED AS A PERCENTAGE OF THE ORIGINAL CARBON.

Temp. °C	30	35	40	50	70	
CO_2	0.10	0.12	0.18	0.19	0.44	
CO	nil	nil	nil	nil	nil	
Volatilised Toluene.	0.20	0.21	0.29	0.34	0.49	
Acidity as D.N. Benzoic Acid.	0.85	0.90	0.92	1.32	1.49	for analysis see p. 121
Acidity as D.N. Cresol	1.27	1.14	0.90	0.72	0.85	do.
% D.N.T. in Nitrobody.	3.1	-	17.7	-	36.2	

From the above data it can be seen that while no CO was detected, the CO_2 figures increase rapidly between 30 and 40°C and again between 50 and 70°C.

The main function of increase in temperature, however,

however, is to increase the D.N.T. content of the M.N.T. (cf. p. 160). The loss of toluene, moreover by volatilisation is doubled over the range 35 to 70°C.

Solid oxidation by-products do not increase with temperature to the same extent as the gaseous products. Whereas dinitrobenzoic acid content is increased by some 60% over the temperature range 35 to 70°C, dinitrocresol is decomposed at the higher temperatures (cf. p. 124) and this no doubt accounts, at least in part, for the increased loss of CO_2 at the higher temperatures.

It will be noted that the gaseous losses are small compared with those in trinitration (p. 66) but that increase in temperature does enhance these losses. It is thus left to the manufacturer to decide the temperature of nitration that will suit his requirements.

Table 3 . Removal of Nitric acid from M.N.T. by Sulphuric acid.

Expt. No.	Temp. °C.	No. of washes.	Ratio by volume of acid to nitrobody.	% H_2SO_4 concentration.	Total acidity of M.N.T. layer as % HNO_3.	R.I. at 20°C.	Corresponding % D.N.T.
1	17	-	-	-	6.3	1.5527	13.0
2	17	1	1:1	80	5.9	-	-
3	50	1	1:1	80	217	1.5562	24.7
4a	50	1)	1:1	80	-	1.5562	24.7
4b	50	1)	1:1	80	1.7	1.5577	29.7
5	50	1	2:1	80	1.6	1.5575	29.0
6	50	1	3:1	80	1.4	1.5577	29.7
7	50	1	4:1	80	1.2	1.5580	30.7
8	50	1	1:1	75	3.9	1.5545	19.0
9	50	1	3:1	76.9	1.95	1.5550	20.7
10	50	1	4:1	76.9	1.58	1.5550	20.7
11	50	1	5:1	76.9	1.28	1.5550	20.7
12	60	1	5:1	76.9	1.00	1.5560	24.0

CHAPTER 8.

REMOVAL OF NITRIC ACID FROM M.N.T.

While investigating oxidation losses it was found that where a substantial excess of HNO_3 was used the resulting M.N.T. contained some 6% HNO_3 in solution. Commercially this is not likely to happen but if it should the removal of this HNO_3 would become a necessity as it would tend to corrode storage tanks and may introduce fire hazards due to oxidation of organic or foreign material.

Acid-free M.N.T. was prepared by washing free of acid followed by vacuum distillation. The refractive index of this purified material was determined before and after solution therein of 6 to 7% HNO_3 (added as 98% HNO_3). There was little or no change in the refractive index, indicating no nitration in the cold. A fixed volume of the acid--containing M.N.T. was treated with varying volumes of of acid and the mixture thoroughly mixed for 5 mins. at room temperature and at 50°C. After allowing the two layers to separate, the M.N.T. layer was analysed for (a) total acidity (since M.N.T. has little affinity for 80% H_2SO_4) and (b) D.N.T. content by refractive index after washing with water and drying. Table 3 summarises the results.

The /

The table shows that provided the acid/ nitrobody ratio is two or greater, the nitric acid concentration can be reduced to a low figure by one wash with 80% H_2SO_4 at 50 °C. With 77% H_2SO_4, nitration ceases at an early stage and thereafter, slow extraction proceeds as demonstrated by the presence of nitric acid in the final spent acid. Increasing the temperature to 60°C encourages further nitration but still not to the same extent as with 80% H_2SO_4. Nitration first occurs and is followed by extraction in all cases - with 80% H_2SO_4 nitration only occurs, as no nitric acid is detectable in the spent acid. Experiments 4 and 5 show the effect of two separate washes (Nos. 4a and 4b) using fresh acid 1:1 in each case and one wash using ratio 2:1 acid/nitrobody (No. 5). It is clear that no advantage is obtained by the former treatment.

The effect of nitrous acid on the removal of nitric acid was next investigated. Solutions of nitrosyl sulphuric acid were prepared by the addition of sodium nitrite to concentrated H_2SO_4 followed by dilution to the required strength. The sodium sulphate that separated was filtered and the remaining acid analysed.

Tests /

Table 4 . Removal of Nitric acid from M.N.T. by Spent Acid.

Expt. No.	Temp. °C.	No. of washes.	Ratio by volume of acid to nitrobody.	Acid Analysis. H_2SO_4	Acid Analysis. HNO_2	Total acidity of M.N.T. layer as % HNO_3.	R.I. at 20°C.	Corresponding % D.N.T.
13	50	1	2:1	76.3	5.5	1.94	1.5555	22.0
14	50	1	3:1	76.3	5.5	1.54	1.5555	22.0
15	50	1	3:1	76.9	-	1.53	1.5550	20.7
16	50	1	5:1	77.0	4.1	1.64	1.5555	22.0
17	50	1	8:1	77.0	4.1	1.30	1.5555	22.0
18	50	1	10:1	77.0	4.1	1.00	1.5555	22.0
19	50	1	2:1	80.4	4.0	1.60	1.5580	30.7
20	50	1	5:1	80.4	4.0	0.86	1.5588	33.3

Tests were carried out as above and the results are tabulated in table 4.

This table showed that nitrous acid had, if anything, a slightly accelerating effect on the rate of nitration (cf. p. 196). Experiment 20 showed the diminution of nitric acid content down to 1% and would represent conditions in commercial practice, i.e. the M.N.T. leaving the plant would receive a wash by T.N.T. spent acid of composition shown in experiment 20 after which the acid would proceed to mononitration.

Increasing the time of contact between spent acid and M.N.T. would lower the nitric acid still in solution (1%) still further.

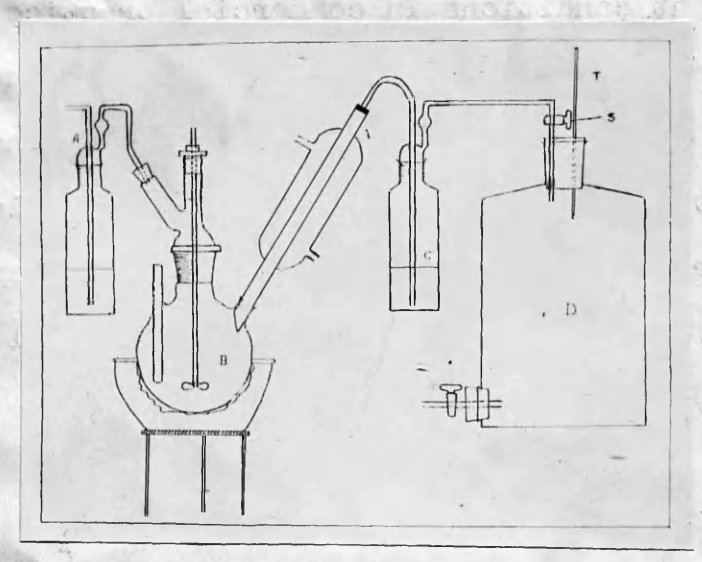


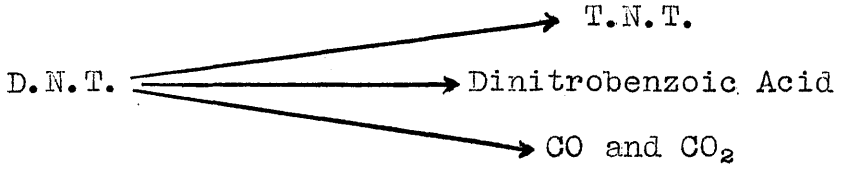
FIG. 7.

CHAPTER 9.

GASEOUS OXIDATION LOSSES IN THE NITRATION OF MONO TO TRINITROTOLUENE.

In the nitration of M.N.T. to T.N.T. the bulk of the oxidation to gaseous products, CO and CO_2 occurs in the di- to tri-nitration stage.

With D.N.T., at least three simultaneous reactions are known to take place.



In order to obtain strictly accurate figures it is necessary to (a) operate in a single phase system. (b) to keep constant the concentration of the nitrating acid. (c) to maintain accurate time and temperature control.

By collecting the gases (diluted with air) in a large evacuated vessel, no confining liquid is necessary. Besides being much easier to work, this has the advantage of eliminating all solubility errors.

A (fig. 7) is a wash bottle containing 30% NaOH through which fresh air from the atmosphere passes before entering the nitrator B. The air sweeps the gas produced through the condenser to the wash bottle C, containing /

containing acidified $KMnO_4$ and thence into the large evacuated bottle D (actual capacity 6.19 litres). Purified nitrogen can be used in place of air, but it was decided to use air for these tests, partly because air may be a factor bringing about oxidation in a commercial plant and partly because the small quantities of gas being produced in this instance necessitated the use of the Haldane apparatus for determining the CO and the CO_2 content of the final mixture in D - which, of course, requires the presence of oxygen.

To keep constant the concentration of oxidising agent would require the use of an infinitely large proportion of nitrating acid which is impossible. A compromise was, therefore, effected by using on an average 2.5 gms. substance under test to 300 gms. mixed acid. In the case of substances readily decomposed, the amount taken was about 0.5 gm. while with the more resistant compounds, such as alpha T.N.T., as much as 6 gms. were used. The acid, raised to 100°C, was added to the substance weighed into B, after which the stopcock S was adjusted to allow a slow stream of air to bubble through A. Gentle stirring was maintained throughout the test. Although this was not strictly necessary in a one phase system, it helped to disengage the /

TABLE 5. GASEOUS OXIDATION PRODUCTS OF THE NITROTOLUENES.

Substance.	Acid Composition			Time in hrs.	% of substance decomposed into		
	H_2SO_4	HNO_3	H_2O		CO	CO_2	Total
o-M.N.T. (temp. 70°C)	80.5	10.7	8.8	2	0.05	0.07	0.12
m-M.N.T. (temp. 70°C)	80.5	10.7	8.8	2	0.03	0.08	0.11
2:4 - D.N.T.	75.0	17.0	8.0	1.5	0.97	2.40	3.37
2:4 - D.N.T.	(83.0	(HNO_2) 9.0	8.0	1.5	nil	0.13	0.13
2:6 - D.N.T.	75.0	17.0	8.0	1.5	1.32	3.04	4.36
D.N.T. from m-M.N.T.	75.0	17.0	8.0	1.5	0.92	3.38	4.30
D.N.T. from o-M.N.T.	75.0	17.0	8.0	1.5	0.88	2.74	3.62
2:4:6 - T.N.T. (alpha)	75.0	17.0	8.0	4	nil	0.34	0.34
2:3:4 - T.N.T. (beta)	75.0	17.0	8.0	4	nil	0.47	0.47
2:4:5 - T.N.T. (gamma)	75.0	17.0	8.0	4	nil	0.10	0.10
2:4:6 - T.N. benzoic acid	75.0	17.0	8.0	1.5	nil	1.19	1.19
2:4 - D.N. benzoic acid	75.0	17.0	8.0	1.5	nil	1.66	1.66
By - product "A"	75.0	17.0	8.0	1.5	nil	0.50	0.50

the bubbles.

About 5 mins. before the expiry of the alloted time, the rate of flow of air was increased in order to fill D at amospheric pressure exactly on time. D was then disconnected and the temperature and pressure noted. The analysis of the contents of D was then carried out in the Haldane apparatus. Table 5 gives the results expressed as a percentage of the original carbon, from the equation

$$\% C = \frac{0.00001603 \times M \times V \times C \times (p - p_v)}{(t + 273) \times n \times W}$$

M = molecular weight of the substance, n = number of carbon atoms, V = volume of air + gas (6190 mls.), C = % CO or CO_2 in V, t = temperature°C, p = pressure (mm. Hg), p_v = vapour pressure in D (saturation pressure), W = weight of substance used (gms.)

DISCUSSION ON TABLE 5.

If the composition of D.N.T. prepared from o-M.N.T. be assumed as 33.4% 2:6-D.N.T. and 66.6% 2:4--D.N.T. (p.48, table 1) the amount of oxidation which 2:6-D.N.T. would give can be calculated as 4.1% - taking the oxidation of 2:4-D.N.T. as 3.37 and that of the mixture as 3.62%. That is 2:6-D.N.T. is oxidised 4.1/3.37 times as fast as 2.4-D.N.T. This was confirmed in the above table by oxidising 2:6-D.N.T. m.pt. 66°C prepared /

prepared from alpha T.N.T. through the 4-amino compound. Moreover, the HNO_2 content of the spent acid was found to be 0.44% for 2:4-D.N.T. and 0.50% for 2:6-D.N.T. thus proving a higher degree of oxidation in the case of the latter.

From the table it is clearly seen that the D.N.Ts. are more sensitive to oxidation than T.N.T. or M.N.T. In particular, the D.N.Ts. from m-M.N.T. are more sensitive to oxidation than 2:4 or 2:6-D.N.T. HNO_2, in the absence of HNO_3, has apparently little effect on the oxidation of 2:4-D.N.T.

Of the three T.N.Ts. mentioned in the table gamma is noteworthy in that very little gaseous oxidation products are formed. Nevertheless, if the solid by-products be considered the oxidation losses in the cases of beta and gamma T.N.Ts. are some two to three times higher than in the case of alpha T.N.T. as can be seen from the following table

TABLE 6. SOLID OXIDATION BY-PRODUCTS.

Substance	% of substance decomposed into solid acidic by-products.
2:4:6-T.N.T. (alpha)	1.38 (as trinitrobenzoic acid).
2:3:4-T.N.T. (beta)	3.14 (as dinitrohydroxybenzoic acid)
2:4:5-T.N.T. (gamma)	3.95 (do.)

The /

The effect of temperature on both the acid and nitrobody phases was next investigated. It has been mentioned (p. 186) that nitrobody preferentially extracted HNO_3 and consequently higher oxidation figures might be expected in the nitrobody phase.

(a) ACID PHASE. 5 gms. D.N.T. + 100 gms. mixed acid (75% H_2SO_4, 17% HNO_3, 8.0% H_2O) were taken as above but the nitrations were conducted at temperatures up to 130°C.

(b) NITROBODY PHASE. 25 gms. 2:4-D.N.T. + 6.68 gms. mixed acid (H_2SO_4 34.3%, HNO_3 63.6%, H_2O 2.1%) were taken in the nitration flask. This amount, corresponding to 21.1% mixed acid in the nitrobody was theoretically capable of nitrating 12.2 gms. D.N.T. The D.N.T. was preheated to the desired temperature, but the small amount of acid was added directly from a pipette without heating. The correct temperature of the mixture was, however, rapidly attained and it is not considered that the addition of such a small amount of cold acid could materially influence the results. The resulting mixture contained only a very small amount of the acid phase at room temperature. This disappeared at higher temperatures. In calculating results, as it was desirable to make them directly comparable to the acid phase results, the D.N.T. equivalent to the HNO_3 added

was /

was taken as the weight of D.N.T. on which the original carbon loss was calculated. Table 7 shows the results.

TABLE 7. LOSSES AS A PERCENTAGE OF THE ORIGINAL CARBON IN THE ACID AND NITROBODY PHASES.

Temp. °C	Losses in acid phase		Losses in nitrobody phase	
	CO	CO_2	CO	CO_2
90	-	-	0.10	0.15
100	1.0	2.4	0.50	0.62
120	1.4	4.0	0.48	0.80
130	1.5	5.2	0.35	1.00

It will be observed that, in general, oxidation in the acid phase is much more marked than in the nitrobody phase. CO_2 in the acid phase increases rapidly with temperature within the range examined, increasing from 2.4% at 100°C to 5.2% at 130°C. CO_2 in the nitrobody phase, although increasing very rapidly with rising temperature between 90 and 100°C from 0.15 to 0.5%, thereafter rises slowly to 1% at 130°C. In the nitrobody phase, CO reaches a maximum at approximately 100°C of 0.5% and thereafter falls slowly to 0.35% at 130°C.

Work was now undertaken on this problem in conjunction with Mr. G.E. Edwards B.Sc. who designed an apparatus to investigate the oxidation losses in the nitration of D.N.T. to T.N.T. and moreover to ascertain /

ascertain if this loss could be minimised by employing anti-oxidants.

The apparatus (fig. 9, - folder at back) was designed to permit the taking of snap samples. It was found that the application to the nitrator of heating and cooling baths gave only very rough control of temperature. As the nitrator was only a 500 cc. capacity quickfit flask, it was not practicable to incorporate a satisfactory cooling coil. The control system shown in fig. 9 , in which part of the nitration mixture was elevated by momentary application of vacuum and cooled in the water jacketed tube A was found to be completely successful. Using this device, the temperature could be maintained to within 1°C throughout the whole nitration. Vacuum was applied when necessary, simply by sealing the air byepass at B with the thumb and forefinger. On releasing this, the cooled nitration mixture was allowed to run back into the flask. The capacity of the cooler was only a small fraction of the total volume of the nitration mixture. Accordingly, the volume of gas lost here was negligible.

The gas collecting and sampling apparatus was first filled with gas oil but this was found to absorb CO_2 very rapidly and was subsequently rejected. After

some /

some experiments it was found that a 30% solution of calcium chloride saturated with CO_2 was suitable for confining the gas.

The gas analysis apparatus was a modified Bone and Wheeler unit operated by compressed air. The method of carrying out a run was as follows.

The nitrator was charged with 50 gms. 2:4-D.N.T. + 300 gms. 100% H_2SO_4 and heated to 105 - 7°C by an oil bath. The oil bath was then removed and 125 gms. mixed acid of composition 60% H_2SO_4, 40% HNO_3 introduced at room temperature through the thermometer pocket. The pocket was immediately replaced. The temperature was adjusted by means of the cooling system to 100°C and maintained there. The heat of reaction kept the temperature at, or about, this figure during the first 15 mins. Afterwards a boiling water bath was used to keep the nitrator at the desired temperature. Immediately the mixed acid was added gas collection was commenced, the gas being drawn into the aspirator C. By regulation of the tap D the gas was maintained at a pressure slightly greater than atmospheric, thus ensuring that in the event of any leakage the gas would not be contaminated with air. Snap samples of gas were collected in the gas burettes E:E and the volume of such samples measured before passing to the gas analysis unit. /

Table 8

Nitrous Acid in Waste Acid before and after addition of Catalysts.

Test No.	Catalyst.	Time of addition. (mins.)	Per cent HNO_2 after Time. Mins.			
			30	45	65	100
2	3:5 dinitro -p-cresol.	60		1.52		2.15
3	do.	60		1.91		2.18
4	2:4 dinitro-benzoic acid.	60		1.50	1.50	
5	Amyl alcohol	60		1.50	2.10	
6	do.	10	1.20			
7	Methyl cyclo-hexanol.	60		1.40	2.20	

unit. It will be noticed that the design of apparatus allows one sample to be drawn while another is being transferred to the gas analysis apparatus. Pressure in the gas sampling tubes was adjusted by taps F (increase in pressure) and G (decrease).

The catalyst (0.5 gms. in every case) was dissolved in 20 gms. of 100% H_2SO_4 and introduced via the tap funnel H at the stated time during the nitration. Introduction of the catalyst at the beginning of the reaction was suitable for studying any change in the gas composition. Introduction after 60 mins., when the gas evolution was slow was more suitable for studying changes in the rate of gas evolution.

Nitrous acid, shown in table 8, was estimated in the reaction mixture before and after the addition of catalyst, by the $KMnO_4$ method. The sample was drawn at tap K.

The volume of gas produced during the first few minutes of the reaction was sufficient to expel air from the apparatus and this obviated the necessity for flushing the apparatus with inert gas before the test. In the initial experiments the gas samples were treated in the gas analysis unit with the following reagents in this order:

(1) /

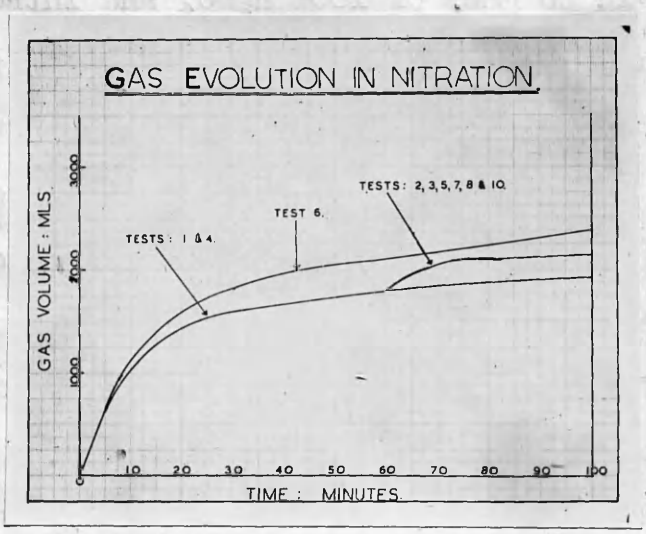

GAS EVOLUTION IN NITRATION.
GAS VOLUME : MLS.
3000
2000
1000
0
TESTS : 1 & 4.
TEST 6.
TESTS : 2, 3, 5, 7, 8 & 10.
10
20
30
40
50
60
70
80
90
100
TIME : MINUTES.

FIG. 10.

Table 9.

Volume and Composition of Gas evolved during Nitration (at N.T.P.)

Test No.	Catalyst.	Time of addition (mins.)		Time. Minutes. 5	10	15	30	45	60	63	65	70	80	100
1	Blank	-	Vol. mls.	585	946	1160	1440	1530	1610					1710
			Gas compsn. CO %	37.9			43.4		43.4					
			CO_2	55.6			55.0		55.0					
2	3:5 dinitro -p-cresol.	60	Vol. mls.	585	936	1180	1410	1530	1570	1670	1740	1790	1845	1860
			Gas Compsn. CO %			32.2					40.3			
			CO_2			54.5					57.7			
3	do.	60	Vol. mls.	585	955	1150	1415	1540	1600	1765	1800	1845	1890	1960
			Gas Compsn. CO %			41.8					39.0			
			CO_2			55.7					59.4			
4	2:4 dinitro beenzoic acid	60	Vol. mls.	585	946	1160	1430	1530	1600	1615	1620	1635	1645	1710
			Gas compsn. CO %			41.1					44.0			
			CO_2			55.5					53.1			
5	Amyl alcohol	60	Vol mls.	540	926	1125	1410	1540	1580	1690	1730		1850	1920
			Gas compsn. CO %			44.4			44.4					
			CO_2			56.2			54.3					
6	do.	10	Vol. mls.	585	955	1260	1630	1800	1890				1980	2140
			Gas compsn. CO %		39.4	41.3								
			CO_2		57.0	56.7								
7	Methyl cyclo- hexanol.	60	Vol. mls.	585	880	1215	1585	1600	1675	1770	1810	1855	1910	
			Gas compsn. CO %			34.2					41.7			
			CO_2			63.0					57.3			
8	do.	60	Vol. mls.	665	990	1170	1450	1575	1645	1710	1755	1810	1925	
			Gas compsn. CO %			44.5					41.7			
			CO_2			53.5					57.6			
9	KI	60	Vol. mls.	665	990	1170	1520	1665	1755		1775	1790	1810	
			Gas compsn. CO %			41.8					41.1			
			CO_2			55.4					56.1			
10	KI	0	Vol. mls.	585	880	1215	1480	1600	1670	1770	1810	1850	1910	
			Gas compsn. CO %	1.86			0							
			CO_2	93.5			99.7							

Table 10 .

Effect of Catalyst on % Carbon Loss.

TEST No.	Catalyst.	Time of Addition. (mins.)	Gas Volume after 80 mins. at N.T.P.	% Carbon Loss.
1	Blank	60	1645	3.72
2	3:5 dinitro p-cresol.	60	1845	4.17
3	do.	60	1890	4.26
4	2:4 dinitro benzoic acid.	60	1645	3.72
5	Amyl Alcohol	60	1850	4.17
6	do.	10	1980	4.48
7	Methyl cyclo-Hexanol	60	1910	4.30
8	do.	60	1925	4.35
9	KI	60	1810	4.09
10	KI	0	1910	4.31

(1) KOH - 30% solution in water (CO_2). (2) alkaline pyrogallol (O_2). (3) Acid ferrous sulphate - saturated solution in H_2SO_4 (NO). (4) Acid Cu_2Cl_2 replaced subsequently by ammoniacal Cu_2Cl_2 (CO). (5) N_2 saturated alcohol (N_2O).

The absorption by (2), (3) and (5) was negligible and in later experiments only (1) and (4) were carried out. Tables 9 and 10 and graph 10 give the results obtained.

DISCUSSION OF RESULTS.

Numerous blanks were carried out, and all agreed closely with the result shown for test 1. Care had to be taken to avoid the use of excess vaseline on the ground glass joints, as this found its way into the nitrator on several occasions and was responsible for high gas volumes.

None of the catalysts employed, decreased the volume of gas evolved during the nitration. While 2:4-dinitrobenzoic acid had no effect, the other substances examined all increased the gas volume by some 200 mls. The effect of potassium iodide on the reaction is interesting. In the experiment in which this was added at the beginning of the reaction, the gas evolved was almost pure CO_2. The fact that the composition did not appear to be effected by the addition /

addition of potassium iodide, after nitration had proceeded for 60 mins., is possibly due to the fact that the main gas evolution is over and only slow oxidation of T.N.T. is occurring which potassium iodide does not affect - in other words, the mechanism of oxidation of D.N.T. differs from that of T.N.T. The acid concentration does not appear to affect to any great extent the gaseous oxidation loss, e.g. table 10 shows a total gaseous loss of 3.72 with an anhydrous acid whereas table 5 shows a loss of 3.37 for an acid containing 8% H_2O.

CONCLUSIONS:

(1) There is a total carbon loss of 3.4% during the nitration of D.N.T. (2:4) to T.N.T.

(2) Acid composition has little effect on the total carbon loss.

(3) None of the catalysts examined reduced the volume of gas evolved.

(4) While 2:4-dinitrobenzoic acid had no effect on the volume of gas evolved, all the other substances examined increased the volume.

(5) The composition of the gas was approximately constant over the time of the reaction even on the addition of "foreign" substances.

(6) /

(6) The average composition of the evolved gas with anhydrous acid is 55.8%CO_2 and 41.7% CO giving a CO_2/CO ratio of 1.33 to 1.

(7) Potassium iodide was the only substance examined which affected the composition of the gas. When this was added at the beginning of the reaction, the gas evolved was almost pure CO_2.

(8) The rate of production of nitrous acid was not affected by any of the compounds examined.

(9) D.N.T. is responsible for the large loss of carbon. As D.N.T. is converted to T.N.T. the loss is appreciably less.

(10) The D.N.Ts. (in particular the unsymmetricals) are much more sensitive to oxidation than M.N.T. or T.N.T.

(11) The rate of oxidation of 2:6-D.N.T. is 30% higher than that for 2:4-D.N.T.

(12) Gamma T.N.T., in contrast to beta suffers little gaseous loss, yet including solid oxidation by-products the losses incurred by both beta and gamma are in excess of those incurred by alpha T.N.T.

(13) The effect of increase in temperature is to increase the rate of oxidation as is to be expected. The gas evolved, however at the higher temperatures is richer in CO_2, the CO remaining approximately constant.

(14) The oxidation in the acid phase is three to five times that in the nitrobody phase.

E X P E R I M E N T A L

S E C T I O N

Part 1.

GASEOUS AND ACIDIC BY-PRODUCTS

SUB - SECTION B

ACIDIC BY-PRODUCTS.

CHAPTER 10.

NITROTOLUENE-SULPHONIC ACIDS.

It is possible that during the nitration of toluene some toluene may be sulphonated and either lost as a sulphonic acid in the acid layer or regained through replacement of the sulphonic by the nitro group thus showing a possible mechanism of nitration.

Sulphonation may precede nitration in the phenol, naphthalene and anthracene series (p. 15). Reference to the literature regarding toluene - sulphonic acids shows the existence of nitrotoluene - sulphonic acids but whether the nitro group is capable of replacing the sulphonic group is not definitely stated.

Toluene-4-sulphonic acid was prepared by heating toluene with 84% H_2SO_4 at 100°C for 7 hours and isolated as the sodium salt (Yield 85%). Constitution was confirmed by preparation of the sulphonamide m.pt. 134-6°C (literature 137°C) via the sulphonyl chloride. With sulphuric acid of lower concentrations little sulphonation occurred e.g. with 75% H_2SO_4 in 6 hrs. at 100°C only 10% sulphonation took place while with 70% H_2SO_4 under the same conditions the toluene was recovered unchanged. As a nitrating acid for toluene contains /

contains in practice about 70% H_2SO_4 it can be seen that no loss of toluene by sulphonation occurs. The possibility of replacing the sulphonic by a nitro group if conditions were such that they allowed of sulphonation, still remained to be investigated.

The action of mixed acids of varying composition on the toluene-4-sulphonate was as follows.

TABLE 11. BEHAVIOUR OF TOLUENE-4-SULPHONIC ACID TOWARDS MIXED ACIDS.

Acid Composition			Temp.	Time of	Product	Derivatives m.pt.	
H_2SO_4	HNO_3	H_2O	°C	Reaction		Chloride	Amide
93.0	1.0	6.0	70-80	1 hr.	2-nitro-toluene-4-sulph.	-	142°C
70.0	5.0	25.0	100	30 mins	do.	-	142-4
76.0	20.0	4.0	100	1 hr.	do.	-	137, mixed m.pt. 139°C
80.0	20.0	-	100	2 hrs.	2:6-di-nitrotol.-4-sulph.	126	198 - 200
88.0	12.0	-	100	7 hrs.	do.	125	202

Incorporating up to 1% water in the last experiment still yielded 2:6-dinitro-4-toluene sulphonate. Tests carried out on toluene-2-sulphonic acid as above gave similar results.

These experiments show that once the sulphonic group enters the toluene nucleus it is not replaceable /

replaceable by nitric acid under normal nitrating conditions. Consequently the formation of toluene sulphonic acids in mononitration would constitute an irrecoverable loss. Fortunately however, the rate of nitration is much faster than that of sulphonation and in mononitration where the temperature is usually about 35°C there is little likelihood of sulphonation occurring. The mechanism of nitration of toluene therefore does not involve the previous sulphonation of the hydrocarbon followed by replacement of the sulphonic by the nitro group.

While investigating the above toluene sulphonic acids, 2:6-dinitrotoluene-4-sulphonic acid was considered to be a likely source of 2:6-D.N.T.. Attempts were made to hydrolyse it using sulphuric acid concentrations ranging from 60 to 96% and temperature from 120 to 200°C with superheated steam, but with no success. A small amount (0.1%) of 2:4-D.N.T. was obtained by steam distillation using superheated steam on the sodium salt of 2:6-dinitro-toluene-4-sulphonate dissolved in 60% H_2SO_4 and heated by an external bath to 120°C to 140°C. The source of the 2:4-D.N.T. is no doubt 2:4-dinitrotoluene-6-sulphonate present as an impurity in the 2:6-dinitro-toluene-4-sulphonate.

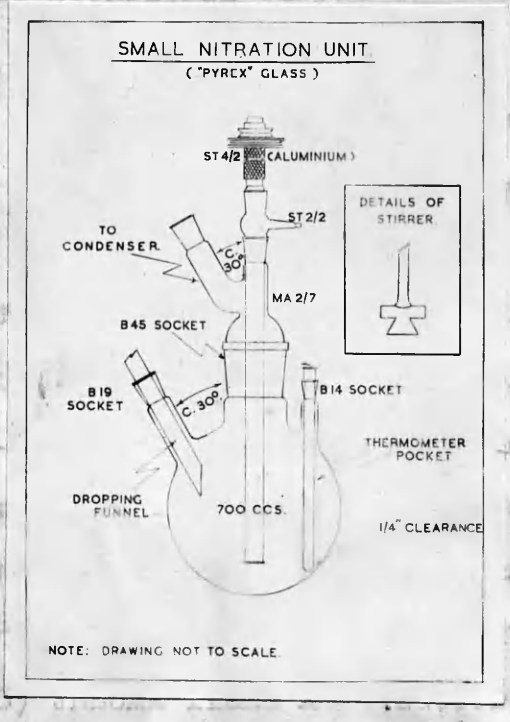

SMALL NITRATION UNIT
("PYREX" GLASS)
ST4/2 (CALUMINIUM)
ST2/2
DETAILS OF STIRRER
TO CONDENSER
C. 30°
MA 2/7
B45 SOCKET
B19 SOCKET
C. 30°
B14 SOCKET
THERMOMETER POCKET
DROPPING FUNNEL
700 CCS.
1/4" CLEARANCE
NOTE: DRAWING NOT TO SCALE.

FIG. 11.

CHAPTER 11.

NITRATION OF THE ISOMERIC M.N.Ts.

Before examining crude T.N.T. (which involves the nitration of M.N.T.) for acidic impurities, it was considered desirable to ascertain the behaviour of the three isomeric M.N.Ts. (para, m.pt. 51.5°C, ortho, C.pt. -4.5°C, meta ex B.D.H., S.P. 15.5°C) on nitration and to evolve a method suitable for estimating the amount of unsymmetrical T.N.Ts. in crude T.N.T. which would be useful in determining non-acidic impurities.

DINITRATION.

50 gms. M.N.T. were heated to 50°C with 120 gms. 90% H_2SO_4 in an all-glass Quickfit vessel (fig. 11) with mechanical stirring. 125 gms. mixed acid (70% H_2SO_4, 21.5% HNO_3, 8.5% H_2O) were added carefully over half an hour allowing the temperature to rise to 70°C, the temperature being maintained there for a total reaction time of two hours. The product was poured into 1500 cc. water, cooled and filtered. It was then washed at 100°C for three 15 mins. periods and finally dried for three hours on the boiling water bath. The melting points of the nitration products were as follows:

Isomer - M.N.T.	Para	Ortho	Meta
D.N.T. m.pt.°C	70 to 71	55 to 66	liquid or low m.pt. solid

The /

The yield of D.N.T. from o-M.N.T. was 84% of theory.

" " " " " p-M.N.T. was 92% of theory.

TRINITRATION.

The dry product (from dinitration) was melted and poured into the nitration flask together with 220 gms. 100% H_2SO_4 and the contents of the flask heated to 100°C with mechanical stirring. 125 gms. mixed acid (60% H_2SO_4, 40% HNO_3) were carefully added, especially over the first 10 mins., maintaining the temperature at 100°C. The addition took half an hour and after a total reaction time of four hours at 100°C, the product was drowned in 1500 cc. water and cooled. After filtering, the T.N.T. was melted, washed 6 times (each wash lasting 5 mins.) at 100°C, in each case with an equal volume of water then dried for 6 hrs. on a boiling water bath. Three hours drying time was found to be a minimum for a further three hours only resulted in an increase of 0.1°C. Finally a set point was determined on each T.N.T. using a thermometer graduated in tenths of a degree from 76 to 82°C (cf. Colver, p. 229).

T.N.T. from	p-M.N.T.	o-M.N.T.	m-M.N.T.
Dry S.P. T.N.T.	80.4 (3 hrs.)		
°C	80.5 (6 hrs.)	80.0 (6 hrs.)	72 to 68(6hrs.)

The set points of T.N.T. from both o- and p-M.N.T. were 0.2°C higher than those recorded by Gibson (J.C.S. /

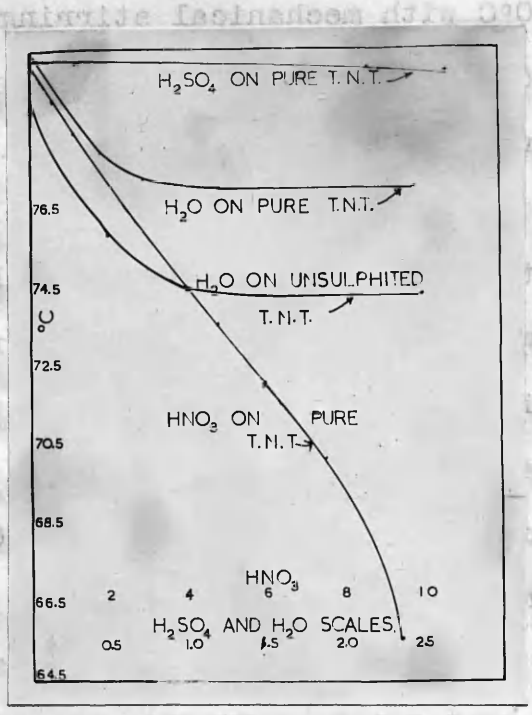

H_2SO_4 ON PURE T. N. T.
H_2O ON PURE T.N.T.
H_2O ON UNSULPHITED T. N. T.
HNO_3 ON PURE T. N. T.
76.5
74.5
°C
72.5
70.5
68.5
66.5
64.5
HNO_3
2
4
6
8
10
H_2SO_4 AND H_2O SCALES.
0.5
1.0
1.5
2.0
2.5

FIG. 12.

(J.C.S. 1922,121,270) but a S.P. of 73.5°C was quoted for T.N.T. from m-M.N.T. The latter result is probably more correct as the m-M.N.T. used in the above experiment had a S.P. on the low side. The T.N.T. from m-M.N.T. gave no definite S.P. and no supercooling occurred.

The yields of alpha T.N.T. from o- and p- M.N.T. were each 88% while the unsymmetrical T.N.Ts. from m-M.N.T. amounted to 80%.

The above experiments were duplicated and gave identical results. Nitration of the isomeric M.N.Ts. was repeated, without washing and drying at the D.N.T. stage to give T.N.Ts. of S.Ps. as follows:

T.N.T. from	p-M.N.T.	o-M.N.T.	m-M.N.T.
Dry S.P. T.N.T. °C.	80.3	79.4	72 to 68

These results showed a slight reduction in S.P. especially with the T.N.T. from o-M.N.T.

As a method of estimating m-M.N.T. varying mixtures of the o-, m- and p- isomers were nitrated as described in the first pages of this chapter. The o-M.N.T. was fixed at 60% and the meta varied at the expense of the para. The m-M.N.T. used in these experiments was synthesised (p. 166). For speedy determinations wet set points (i.e. S.Pt. of water saturated T.N.T.) proved to be accurate. Fig. 12 shows /

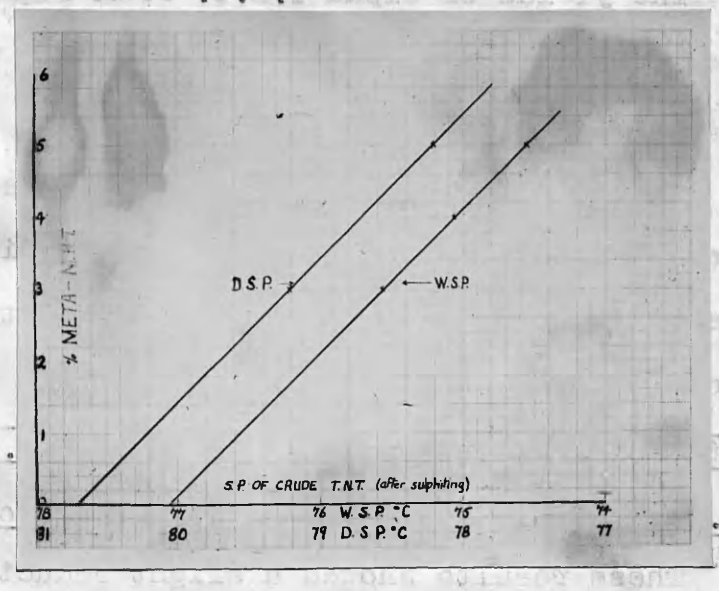

6
5
4
3
2
1
0
% META-N.P.T.
D.S.P.
W.S.P.
S.P. OF CRUDE T.N.T. (after sulphiting)
78
81
77
80
76 W.S.P. °C
79 D.S.P. °C
75
78
74
77

FIG. 13.

shows the effect of H_2SO_4, HNO_3, H_2O on the S.Pt. of T.N.T. Complete saturation of pure alpha T.N.T. by water results in a lowering of S.Pt. of 3.5°C. This figure has been tested repeatedly, the margin being 3.5 - 3.55°C. In converting a wet S.Pt. to a dry S.Pt. however, 3.65 - 3.70°C is added to the S.Pt. of the crude T.N.T. (Ministry of Munitions, Tech. Recs. No.2 p. 99), the additional 0.15°C being possibly due to tetranitro methane which is known to be formed in small amount in the trinitration stage. Each T.N.T. was sulphited to maximum set point (p.135) - in all cases 80.71°C - which was taken to correspond to 0% meta isomer in M.N.T. Table 12 and fig. 13 show that 1% meta isomer in M.N.T. lowers S.Pt. of final T.N.T. 0.5°C.

TABLE 12. EFFECT OF THE META ISOMER IN M.N.T. ON THE FINAL S.P. OF THE T.N.T.

% meta isomer	- Set Points Wet	Dry	After sulphiting to max. set point, dry S.P. °C
3	75.56	79.21	80.71 (W.S.P.=77.06)
4	75.06	78.71	80.71
5	74.56	78.21	80.71

From the work described above it is possible to draw the following conclusions.

(1) p-M.N.T. yields pure 2:4-D.N.T. at the dinitration stage. This D.N.T., in turn, gives a high grade T.N.T. S.P. 80.40°C, but impurities are also present. The colour of the T.N.T. is better than that from ortho.

(2) /

(2) o-M.N.T. yields a mixture of D.N.Ts. at the dinitration stage. The D.N.Ts. give a T.N.T. of S.P. 80.0°C indicating the presence of impurities.

(3) The separation, washing and drying at the dinitration stage leads to a purer T.N.T. in both of the above cases.

(4) A minimum drying time of three hours at 100°C is required for accurate S.P. determinations.

(5) It is possible to estimate m-M.N.T. by nitration to T.N.T. (under specified conditions) and determining the wet set point after washing the T.N.T. free of acidic bodies. Each fall of 0.5°C below 77.06 indicates 1% meta isomer in the original M.N.T.

CHAPTER 12.

RENITRATION AND BY-PRODUCT "A" FORMATION.

Since T.N.T. from p-M.N.T. had S.P. 80.5°C indicating the presence of impurities, possibly D.N.T., it was desirous to find the maximum S.P. obtainable on nitration. Consequently, the T.N.T. from each of the isomeric M.N.Ts. was renitrated as below.

T.N.T. prepared from p-M.N.T. as on p. 79 was melted and transferred to the nitration flask. To it were added 180 gms. 100% H_2SO_4 and the mixture heated to 100°C with stirring. 80 gms. mixed acid containing 60% H_2SO_4, 40% HNO_3 were added slowly to maintain the temperature at 100°C, where it was maintained for a total reaction time of three hours. The changes in S.P. after a series of these nitrations on the T.N.T. from p-M.N.T. were as follows:

	Experiment No.			
	1	2	3	4
Dry S.P. T.N.T. °C	80.54	80.56	80.48	80.50
Dry S.P. on renitration	80.36	80.14	80.30	80.10

Attention is drawn to the drop in S.P. of T.N.T. which is due probably to the formation of some soluble by-product. It is to be noted, however, that on renitrating a T.N.T. from technical M.N.T. an increase in S.P. is usually obtained for the first renitration.

In /

In connection with the S.Ps. after renitration, the drying time was more important, probably due to the presence of tetranitromethane, since a minimum of five hours at 100°C was required e.g. after three hours drying time the S.P. was only 79.97° but after five hours it was 80.29°C and after six hours 80.30°C.

After trying a number of solvents (cf. p. 94) it was found that the impurity causing the lowering of the S.P. was insoluble in chloroform. Extraction of the T.N.T. from p-M.N.T., after a renitration, with chloroform in a Soxhlett gave 0.30% of a white compound m.pt. 270°C (decomposition). The T.N.Ts. from o- and m-M.N.T. gave no such compound under similar conditions. The above experiments were repeated but only a portion of the T.N.T. from o- and m-M.N.T. was tested for the above impurity, hereafter designated by-product "A", after the first renitration. The remainder was subjected to a further renitration, lasting three hours, with fresh acid of the same concentration. The T.N.T. from o-M.N.T. gave 0.25% by-product "A" m.pt. 280°C (decomposition). The T.N.T. from m-M.N.T., on the other hand, gave no by-product. In no case was this impurity detected at the trinitration stage.

It is concluded from the above experiments that (1) S.P. of T.N.T. from p-M.N.T. on 3 hrs. renitration /

renitration is lowered due to the formation of 0.30% by-product "A".

(2) T.N.T. from o-M.N.T. yields 0.25% of the same by-product after six hours renitration.

(3) The T.N.T. from m-M.N.T. yields no such product after six hours renitration.

(4) The impurities present in T.N.T. from o-M.N.T. appear to inhibit the formation of this by-product, e.g. 2:6-D.N.T. or other isomers.

(5) The isomeric unsymmetrical T.N.Ts. apparently play no part in the formation of by-product "A".

(6) Since the isomeric M.N.Ts were of high purity, the precursor of by-product "A" cannot be formed prior to the M.N.T. stage.

(7) Conclusion (1) suggests that by-product "A" either forms a soluble addition product with T.N.T. or is itself soluble to some extent in T.N.T.

CHAPTER 13.

FORMATION OF AN ADDITION COMPLEX BETWEEN T.N.T. AND TRINITROBENZOIC ACID (T.N.B.A.).

Persuing the last conclusion in the previous chapter further, trinitrobenzoic acid anhydride and T.N.B.A. are impurities which are naturally looked for under renitration conditions. No trace of these compounds was detected, however in T.N.Ts. which had been prepared from the isomeric M.N.Ts. by nitration at 100°C. Accordingly, experiments were carried out to determine (a) the ease of formation of trinitrobenzoic acid anhydride and (b) possibility of complex formation between T.N.B.A. and T.N.T.

(a) The only reference in the literature to trinitrobenzoic acid anhydride is in J.C.S. 1895,67,600 where Sudborough mentions it as a by-product in the preparation of trinitrobenzoyl chloride using PCl_5 together with the oxychloride. It is described as a white compound m.pt. 280°C (d.)

Sudborough's experiment was repeated on 1 gm. T.N.B.A. but no high melting compound was isolated and consequently attempts were made to prepare it by other means.

(1) 1 gm. T.N.B.A. m.pt. 215°C (Org. Synth., Gilman, Vol.1 p. 528) /

Vol.1 p. 528) together with 10 cc. 20% oleum were refluxed for seven hours on a boiling water bath. The solution which was colourless at first, on heating turned red. On drowning the solution in water no solid separated. Extraction of the solution with ether, however, gave an acidic compound m.pt. 206°C (d.) which proved to be unchanged T.N.B.A.

(2a) 1 gm. T.N.B.A. together with 13 cc. acetic anhydride were refluxed for seven hours at 100°C. The solution, when the trinitrobenzoic acid first dissolved, was yellow in colour but on heating, it turned red. On drowning in water, a red oil separated which, when crystallised from alcohol, gave a brown solid m.pt. 113°C. Concentration of the acetic acid solution gave trinitrobenzene m.pt. 121°C. The experiment was repeated using redistilled acetic anhydride to give an identical result.

These two methods were attempts at dehydrating T.N.B.A. As experiment (1) gave no positive result, it is unlikely that any anhydride would be formed under renitration conditions.

A final attempt was made to prepare the anhydride through the acid chloride m.pt. 158°C and the sodium salt of T.N.B.A. The chloride was prepared according to Sudborough (loc.cit.) as thionyl chloride and phosphorus oxychloride were not reactive. The

sodium /

sodium salt was prepared in alcoholic solution and precipitated by petroleum ether (b.pt. 60 - 80°C) and proved extremely explosive. The chloride was fused and kept at 168°C in a test tube while the sodium salt was cautiously sprinkled in. The reaction proceeded smoothly for about 5 mins. then the mixture exploded. For the next attempt, the chloride and the sodium salt were both dissolved in acetone, mixed and the solution refluxed for 1 hour, but only a tar resulted.

Since trinitrobenzoic acid anhydride proved so difficult to prepare under conditions akin to those in nitration and what is more important since the combustible and reduceable nitrogen would be identical for this compound - which is not the case with by-product "A" (p. 103) - there can be no doubt that "A" is a substance altogether different from the acid anhydride.

(b) The solubility of trinitrobenzoic acid was first determined. A known weight (excess) of T.N.B.A. was added to 50 cc. chloroform and kept at room temperature for two hours with frequent shaking. The mixture was run into a weighed sintered glass crucible under suction. After drying in a vacuum desiccator, the crucible was weighed and the solubility determined. Solubility by volume at 18.5°C = 0.22 gms./100cc. $CHCl_3$.

Solubility /

solubility by weight at 18.5°C = 0.14 gms./100gms. $CHCl_3$

A series of experiments were carried out to determine if any addition compound was formed and if so the necessary proportions of reactants required.

Varying weights of T.N.T., S.P. 80.4°C, and T.N.B.A. were mixed and heated in a test tube until fusion occurred. They were maintained in the molten state for a short period then poured on to a watch glass, and after solidifying a melting point was taken before and after extraction with chloroform.

(1) 0.25 gm. T.N.T. + 0.25 gm. T.N.B.A. m.pt., partially melts 83-4°C; shrinks 127-8°C; melts 165 - 180°C. After treatment with chloroform there is an insoluble portion m.pt. 61-3°C.

(2) 0.25 gm. T.N.T. + 0.50 gm. T.N.B.A. The product behaved as in (1). The insoluble portion in chloroform melted 215°C (d.) while the soluble portion melted 61-3°C

(3) 0.25 gm. T.N.T. + 0.75 gm. T.N.B.A.)
(4) 0.25 gm. T.N.T. + 1.00 gm. T.N.B.A.) behave as in (1) and (2).

(2a) 0.50 gm. T.N.T. + 0.25 gm. T.N.B.A. m.pt., partially melts 58°C, further change 64 to 70°C and melts 120 to 140°C. After treatment with chloroform, there is an insoluble portion m.pt. 210°C (d.) and a soluble portion m.pt. 61-7°C.

(3a) 0.75 gm. T.N.T. + 0.25 gm. T.N.B.A. m.pt., partially /

partially melts 74-5°C and to a clear liquid by 140°C. After treatment with chloroform there is an insoluble portion m.pt. 215°C (d) and a soluble portion m.pt. 76-8°C.

(4a) 1.0 gm T.N.T. + 0.25 gm. T.N.B.A. m.pt., partially melts at 76°C and completely by 130°C. Treatment with chloroform gives an insoluble portion m.pt. 215°C and a soluble portion m.pt. 76°C.

The result of these experiments show that in all cases unchanged T.N.B.A. m.pt. 215°C was recovered. In the experiments with an excess of T.N.B.A. a small amount of a compound soluble in chloroform and having a m.pt. 61-3°C was isolated.

Consequently, 25 gms. T.N.T., contained in a small beaker, were melted and 0.1 gm. amounts of T.N.B.A. added at intervals. After each amount had dissolved the S.P. was determined, the whole procedure occupying about three days. Table 13 shows the results.

Further addition, beyond 3.65% T.N.B.A., resulted in some material remaining undissolved. The solubility of T.N.B.A. in T.N.T. was estimated about 3.7%. On pouring the molten T.N.T., containing the T.N.B.A., into 100 cc. chloroform no T.N.B.A. separated. This indicated the formation of a complex or alternatively the decarboxylation of the T.N.B.A.

The /

The figure of 3.7% represented a saturated solution of T.N.B.A. in T.N.T. at 100°C for on standing overnight a small amount of T.N.B.A. separated.

TABLE 13. SET POINT OF T.N.T. - T.N.B.A. MIXTURES.

	S.P. °C	Remarks
T.N.T.	80.3	
T.N.T. + 0.38% T.N.B.A.	80.08	
" + 0.76% "	79.92	
" + 1.14% "	79.75	2° supercooling.
" + 1.53% "	79.52	2.5° supercooling.
" + 1.92% "	79.17	2.5° "
" + 2.35% "	79.12	1.6° "
" " "	78.80	2.5° "
" + 2.77% "	78.71	
	78.65	
" + 3.21% "	78.72	1.0° "
" + 3.65% "	78.48	

By fractional crystallisation of the final fractions from chloroform a small amount of a compound m.pt. 61°C was obtained but which showed no evidence of containing a carboxyl group. Extraction of the T.N.T. solution containing 3.7% T.N.B.A. with 2% carbonate solution followed by acidification and ether extraction gave no T.N.B.A. Accordingly 1 mol 2:4:6-trinitro benzene was fused with 1 mol alpha T.N.T. and the product crystallised from alcohol to give a compound m.pt. 61°C. /

m.pt. 61°C. Thus, the T.N.B.A. had undergone decarboxylation to trinitrobenzene which combined with T.N.T. to form an additive compound and this explained why no T.N.B.A. was found in the T.N.T. Such a reaction is not likely where acid is present (p. 99) but it is highly possible during the latter stages of the washing process.

CHAPTER 14.

BY-PRODUCT "A" - ANALYSIS.

In chapter 12 it was mentioned that during the renitration of alpha T.N.T. a white compound m.pt. 280°C (d.), designated by-product "A" was isolated by virtue of its insolubility in chloroform. Traces of impurities tended to inhibit its formation since it was not formed so readily from the T.N.T. derived from o-M.N.T. Chapter 13 showed that it was not formed from T.N.B.A., consequently a detailed analysis was undertaken.

PURIFICATION.

The crude, water washed, dried T.N.T. is extracted with chloroform or carbon tetrachloride in which solvents "A" was insoluble - a Soxhlett apparatus gave the best results yielding a product which when crystallised from acetone had m.pt. 280°C, (d.).

It may be mentioned at this stage that all melting points relating to "A" are with decomposition unless otherwise stated. Determinations of melting points in closed instead of open capillaries gave little or no difference save that the decomposition was less marked in the closed tube.

SOLVENTS.

"A" /

"A" was practically insoluble in benzene, carbon tetrachloride, chloroform and petroleum ether.

It was partially soluble in 90% formic acid and in fuming nitric acid; an indication of its great stability towards acid. It was extremely soluble in acetone, ether, decalin, dioxan, benzyl, amyl and ethyl alcohols, cyclohexanol. Acetone-petroleum ether was tried and gave excellent results as long as acetone was in excess.

The solubility of "A" in acids of composition 82% H_2SO_4, 2.5% HNO_3, 15.5% H_2O (No. 1 acid) and 72.5% H_2SO_4, 12.0% HNO_3, 15.5% H_2O (No. 2 acid) was determined as follows. 1 gm. of purified "A" was refluxed with 50 cc. of each of those acids at 100°C for four hours, filtered, given three water washes and dried in the steam oven. Table 14 shows the results obtained.

TABLE 14. SOLUBILITY OF "A" IN MIXED ACID.

Acid No.	Solubility per 100 cc. at 100°C
1	0.28 gms.
2	0.29 gms.

Considerable difficulty was experienced in filtering the above acids. Glass sinters were used initially but finally they were abandoned in favour of Gooch crucibles. The results show that the acid composition does /

does not affect the solubility of "A".

CRYSTALLISATION.

The compound could be crystallised from benzyl alcohol, acetone, glacial acetic acid, formic acid and fuming nitric acid. The two latter solvents yielded microscopic crystals which readily lost their solvent of crystallisation. Slow evaporation of an acetone solution of "A" gave large brown crystals which readily became amorphous.

There was wide variation in the melting points of varieties of "A" crystallised from different solvents indicating the presence of (1) solvent of crystallisation. (2) the presence of isomers, each solvent exerting a preferential effect. (3) decomposition in certain solvents.

The crystals from benzyl alcohol had a m.pt. 198-200°C. Drying the crystals under vacuum raised the melting point to 228°C, the crystal structure being still retained. It was difficult to remove the last traces of benzyl alcohol because of its high boiling point but the crystals m.pt. 228°C, without doubt contained benzyl alcohol of crystallisation because (1) there was a loss of weight on drying corresponding to the molecular weight of benzyl alcohol - 110. (2) the equivalent of the crystals was 110 in excess of the /

the amorphous powder (obtained on drying), m.pt. 250°C. (3) the odour of benzaldehyde was distinguishable on treating the crystals with alkaline permanganate.

The concentration of the mother liquor from the benzyl alcohol crystals yielded a dark resin which may be of value.

The crystals from formic acid and fuming nitric acid melted at 238°C but as the crystals became amorphous the melting point rose to 250°C. The solvent, in this case, did not appear to be associated with the compound so that partial decomposition might have occurred or alternatively the 250°C melting point form was isomeric with the 280°C melting variety.

SALTS.

The sodium salt was prepared as follows: "A" was dissolved in ether containing 20% ethyl alcohol and the solution stirred vigorously while alcoholic caustic soda was added slowly. Addition was continued until the ether showed a faint red colour which persisted on stirring for 10 mins. Cooling, together with concentration if necessary, yielded brown needles m.pt. 107°C. Excess of caustic soda gave a brilliant red colour to the resulting crystals. The above corresponded to the normal salt but the acid sodium salt was also prepared by adding half the above amount /

amount of caustic soda.

The ammonium salt was prepared by taking a suspension of "A" in distilled water and boiling the solution. Dilute ammonia was added until a slight excess was present. Boiling the solution was continued until no ammonia could be detected, after which the solution was filtered hot and on cooling, red crystals separated m.pt. 238°C.

As a check on the acid equivalent, attempts were made to prepare the silver salt. To a clear solution in water of the ammonium salt was added decinormal silver nitrate solution. A pink flocculent precipitate resulted m.pt. 218°C. On adding alcohol to the filtrate, a white compound m.pt. 246°C was obtained. Concentrating the filtrate from the latter gave a greyish precipitate. These salts, however, were insoluble in most solvents and in nitric acid.

Boiling a mixture of "A", water and a solution of lead nitrate yielded a flocculent white precipitate of the lead salt which was extremely explosive. Incidentally, all the previous salts were highly explosive also. The lead salt could also be prepared by treating a solution of the sodium or ammonium salts with a solution of lead acetate.

VARIETIES OF "A".

A compound m.pt. 280°C was obtained by extraction with chloroform in a Soxhlett. Since this might contain inorganic matter purification was considered necessary. Crystallisation from acetone, followed by drying to obtain the amorphous form gave a brownish product m.pt. 272°C. Moreover, a peculiar odour, hinting at some form af decomposition of either the acetone or "A" was always associated with these crystallisations.

Benzyl alcohol crystals m.pt. 228°C, after drying three hours on the water bath followed by further two hours at 120°C to remove the last traces of benzyl alcohol, gave a brown amorphous powder m.pt. 250°C.

Crystals from formic or fuming nitric acids had m.pt. 238°C which on drying rose to m.pt. 250-2°C, but the colour of the products was dark and unlike that obtained by precipitation from alkali.

Dissolving "A" in cold alkali followed by acidification gave a white product m.pt. 252°C. This variety on heating with 98% H_2SO_4 for 4 to 8 hrs. at 100 to 130°C produced the 280°C melting point variety, whereas crystallisation from fuming nitric acid produced the 252°C melting point form. It is extremely probable that the two varieties of m.pt. 252 and 280°C are isomers.

Boiling /

Boiling "A" in suspension in distilled water for short periods up to half an hour yielded a white product m.pt. 252°C together with a small amount m.pt. 238°C. Boiling for periods up to two hours gave a flocculent product m.pt. 217°C. If the water, however, contained small quantities of mineral acid, the rate of decarboxylation was much reduced and in the presence of concentrated acid at 100°C was practically non existent.

The ammonium salts prepared from the 280, 272 or 217°C melting point varieties each gave a m.pt. 238°C and it was deduced from this that the dicarboxylic acid forms of "A" (m.pts. 280 and 272°C) were first converted to the monocarboxylic acid form m.pt. 217°C which then formed the ammonium salt. Acidification of a solution of the ammonium salt yielded a reddish brown product m.pt. 214°C which on purification with animal charcoal proved to be identical with the monocarboxylic acid form by mixed melting point determination. Acidifying the sodium salt gave similar results.

All compounds of m.pt. $\geq$ 217°C, related to "A" were acidic in character. Attempts to detect carbon dioxide in the different varieties were not successful using lime water but some success was obtained using baryta, all the products of melting point greater than 217°C giving carbon dioxide. The test was carried out as follows: Air, freed from CO_2 by passage through 50% NaOH /

NaOH followed by soda lime, was led into a suspension of the compound in air-free distilled water which was kept gently boiling. The vapours were drawn off by a water suction pump through a trap tube and finally through decinormal baryta. The method was made quantitative by employing a technique similar to that employed in determining the weight of carbon dioxide evolved during combustion. It was then shown that the dicarboxylic acid form of "A" (m.pt. 280°C) lost the equivalent of one carboxyl group to give the mono-carboxylic acid form m.pt. 217°C.

In concentrated sulphuric acid solution at 180°C, "A", m.pt. 280°C rapidly dissolved and in a very short time the solution turned yellow. In the space of 90 mins. the CO_2 evolved was equivalent to the loss of the two carboxyl groups. On cooling the solution, orange coloured crystals separated in small yield. The melting point of these crystals was greater than 360°C and they appear to be more complex than "A" itself.

A similar test, in which "A" was heated alone in an oil bath at 200°C and the vapours drawn over starch iodide papers moistened with glycerine and finally through water, was carried out over a period of eight hours. The starch iodide paper showed a blue colouration /

colouration and the presence of nitrous acid in the water was shown colorimetrically with Griess' reagent. Extraction of the charred mass remaining in the test tube with ether gave a minute amount of a red substance m.pt. 176°C. Employing less drastic conditions, resulted in only a darkening of "A".

For analysis, the following varieties were chosen: 250°, 217°, representing the di- and mono-carboxylic acid forms of "A". Tests for the elements indicated the presence of carbon, hydrogen and nitrogen but no sulphur.

ANALYSIS.

(a) Carbon, Hydrogen and Nitrogen. The hemi-macro method of Rodger and Johnstone (J.S.C.I. 1935,54,46T) was used and gave consistent results.

(b) Nitro Groups The percentage nitro groups was estimated by titanous chloride (Cumming, Hopper and Wheeler, Syst. Org. Chem. p. 218). Pure p-nitraniline was used for standardisation purposes and as chlorination was considered likely in some cases, occasional checks were performed with titanous sulphate.

(c) Equivalents. These determinations were carried out using N/10 and occasionally N/20 alkali (indicator phenolphthalein), on the same solution as (c). Some of the compounds examined gave anomalous results probably /

probably due to nitrolic acid formation e.g. on compound m.pt. 238°C equivalents of 63, 195, 222 were obtained. To check the values obtained in table 15 attempts were made to determine the equivalents through the formation of a silver salt but they proved unsuccessful. A further attempt was made by estimating the ammonia evolved on decomposition of the ammonium salt. However, since polynitro compounds are prone to decompose in the presence of strong alkali with the liberation of ammonia this method was also discarded.

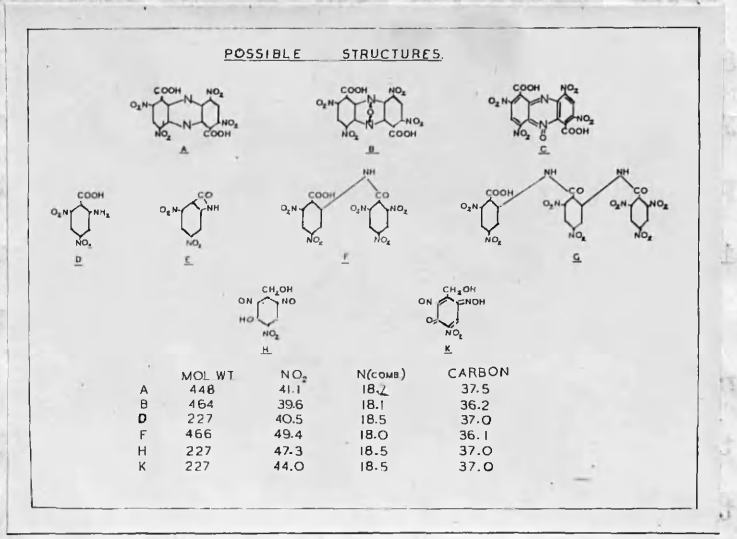
(d) Molecular Weights. These were determined by elevation of the boiling point of acetone but are far from accurate as only small elevations were obtained. The determinations were carried out with 50 cc. solvent and 0.2 to 0.6 gms. material when the corresponding increase in boiling point was of the order of 0.02 to 0.08°C. Other methods were tried, notably Menzies' vapour pressure method but to no advantage. Different solvents such as phenol, thymol, dibenzyl, bromoform, carbon bisulphide, ethyl acetate, methyl alcohol, cyclo hexanol, dioxan etc. were used in place of acetone but again to no advantage. Determinations involving the lowering of the freezing point of glacial acetic acid yielded no better results nor did Rast's camphor /

TABLE 15. ANALYSIS OF MAIN VARIETIES OF BY-PRODUCT "A".

Substance m.pt. °C	250	250	217
How obtained	alkali-acid treatment.	crystallised from formic acid.	water reflux
Appearance	needles	colourless needles.	colourless needles.
ANALYSIS.			
% C	37.75	37.53	38.30
H	1.59	1.94	1.67
N	17.50	17.30	19.60
O	43.16	43.23	40.43
% NO_2	42.00	44.40	49.40
Red. N	12.80	13.50	15.00
Mol. Wt.	430	413	416
Equiv.	224	233	435

camphor method e.g. on determining molecular weights of compound m.pt. 250 from benzyl alcohol, Rast's method gave a value approximating to 400; depression of the freezing point of glacial acetic acid gave 95 and elevation of the boiling point of dioxan gave 450.

Table 15 gives the results pertaining to the purest forms associated with "A" and incidentally those which gave the most reliable data. The high melting variety of "A" was shown clearly to be a dicarboxylic acid, produced possibly by oxidation of the methyl group in T.N.T. (see next chapter). A molecular weight of approximately 400 indicates the presence of two benzene rings, the linkage being through nitrogen since the ratio of reducible nitrogen (by $TiCl_3$) to combustible nitrogen is in the neighbourhood of 0.75. Decarboxylation of this variety yields the mono carboxylic acid form m.pt. 217°C. The structure finally suggested for "A" m.pt. 280°C was that of a phenazine oxide - structure B or C, fig. 14 p. 104. Since phenazines are highly coloured bodies an oxide or azoxy structure has to be assumed.



	MOL WT	NO_2	N(COMB)	CARBON
A	448	41.1	18.7	37.5
B	464	39.6	18.1	36.2
D	227	40.5	18.5	37.0
F	466	49.4	18.0	36.1
H	227	47.3	18.5	37.0
K	227	44.0	18.5	37.0

FIG. 14

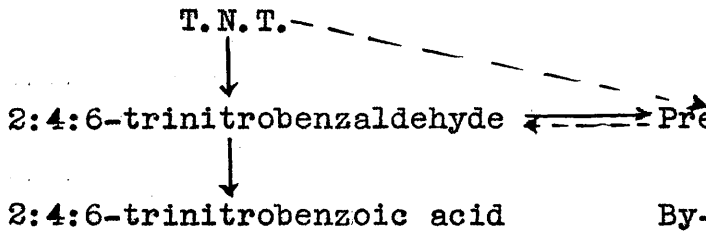
CHAPTER 15.

SYNTHESIS AND THE MECHANISM OF FORMATION OF BY-PRODUCT "A".

Previously (p. 84) it had been shown that, on nitration, p-M.N.T. gave "A" most readily followed by o-M.N.T. : m-M.N.T., on the other hand, gave no "A". It was therefore concluded that 2:4-D.N.T. on nitration yielded "A" as a by-product, 2:6-D.N.T. apparently inhibiting the reaction. Time appears to be the predominant feature of "A's" production since a renitration is required. The affinity of the nitrobody for HNO_3 (p. 186) may also play a part.

In the previous chapter it was seen that "A" was a dicarboxylic acid involving two aromatic nuclei, linked through nitrogen and from the analysis a phenazine oxide structure was suggested (B or C, fig. 14). Assuming this structure, the most likely synthesis would be by the condensation of two mols of 2:4:6-trinitrobenzoic acid but this was shown to be unlikely in chapter 13 where the possibility of trinitrobenzoic acid anhydride was also ruled out. Moreover, trinitrobenzoic acid is stable to concentrated H_2SO_4 and mixed acids under normal conditions and at temperatures up to 100°C. Since trinitrobenzoic /

trinitrobenzoic acid does not appear to be the precursor of "A", the possibility of 2:4:6-trinitro benzaldehyde undergoing condensation and oxidation was considered. The more likely theories, therefore are based on a series of reactions such as the following:



In support of the above scheme, it was shown that "A" could be produced in small yields from trinitrobenzaldehyde in 2 to 6 hrs. at 120°C by the action of concentrated H_2SO_4. Similarly, 2:4-dinitro benzaldehyde produced "A" by condensation in the presence of concentrated H_2SO_4 followed by nitration.

2:4-dinitro and 2:4:6-trinitrobenzaldehydes react readily with 2:4-dinitrophenylhydrazine to form the corresponding hydrazones. These have a yellow -orange colour and have m.pt. 251° and 193°C respecively. As the yields of these compounds are claimed to be quantitative, it was decided to trace the decomposition of the aldehydes by gravimetric estimations of the 2:4-dinitrophenylhydrazones after varying periods of time. The method adopted was that laid down in the B.D.H. handbook, 8th, edt. 1941.

Approximately /

Approximately 4×10^{-3} molar quantities of the aldehydes were dissolved in 10 ml. 85% H_2SO_4 and digested under a nitrogen seal at 95°C. At specified intervals, 1 ml. was pipetted off and run into 5 ml. reagent which consisted of a saturated solution of 2:4-dinitrophenylhydrazine in 2N HCl. The hydrazones were precipitated immediately, and after keeping one hour, they were filtered through Gooch crucibles, washed once or twice with 2N HCl and finally with water. The crucibles were dried in the water oven for 30 mins. before weighing. The melting point of each precipitate thus obtained was also taken. The results are calculated as percentages of the original aldehyde taken. (Factors: Hydrazones x 0.521 = dinitro compound, x 0.573 = trinitro compound). Table 16 gives the results, the melting point of the hydrazone precipitates being given in brackets.

It was observed during these experiments that while the 2:4-dinitroaldehyde solution remained clear, the 2:4:6-trinitroaldehyde solution became turbid after 4 hours and a precipitate formed after 10 hrs. This precipitate ("A") was determined on an aliquot part of the solution and amounted to 21.7% of the original weight of the aldehyde taken.

TABLE 16 /

TABLE 16. STABILITY OF NITROALDEHYDES TO 85% H_2SO_4.

Time at 95°C		% Remaining in Solution.	
Hours	Mins.	Dinitroaldehyde	Trinitroaldehyde.
	10	100.0 (251°C)	78.8
	35	88.0 (251°C)	-
	30	-	68.6 (193°C)
1	40	86.2	-
2	45	-	56.4
3	50	78.1 (250°C)	-
5	55	-	42.6 (193°C)
6	30	-	32.8
10	-	74.3	21.8

As the samples used in this work were several weeks old, it was thought that the aldehyde content of each would probably be low owing to isomerisation - particularly as both samples were discoloured. The trinitro compound was, in fact, quite dark in appearance. A separate determination, however, of the aldehyde content was made by precipitating the 2:4-dinitrophenylhydrazones from aqueous alcoholic solution. The results were: Dinitroaldehyde - 103%; Trinitroaldehyde - 102%. It is evident from the foregoing that these polynitro aldehydes are stable on keeping at ordinary temperatures. From table 16 the trinitrobenzaldehyde /

trinitrobenzaldehyde is shown to be the more unstable in hot sulphuric acid solution.

It is difficult to see how "A" can be produced from trinitrobenzaldehyde in the presence of free HNO_3 since the aldehyde is in all probability oxidised immediately it comes into contact with mixed acids. The stability of trinitrobenzaldehyde towards mixed acids was therefore investigated.

0.5 gm. trinitrobenzaldehyde, m.pt. 117-8°C was dissolved in 5 cc. mixed acid and heated at various temperatures for periods up to 5 hrs. The presence of "A" or trinitrobenzoic acid was tested for by solubility in carbon tetrachloride followed by boiling with water when trinitrobenzoic acid gave trinitrobenzene m.pt. 121°C and "A" gave the mono-carboxylic acid form m.pt. 217°C (d.). No by-product "A" or trinitrobenzoic acid was detected in five hours at temperatures below 85°C. At temperatures above this, however, trinitrobenzoic acid increased with temperature and nitric acid concentration. All samples gave precipitates with 2:4-dinitrophenylhydrazine indicating unchanged aldehyde.

2:4-dinitrobenzaldehyde, on the other hand, produces the corresponding acid within 5 hrs. at 85-7°C with 6% HNO_3, 88% H_2SO_4 and is therefore less stable towards mixed acids than the trinitroaldehyde. This

is /

is in contradistinction to the effect of 85% H_2SO_4.

TABLE 17. THE ACTION OF MIXED ACIDS ON TRINITROBENZALDEHYDE.

Acid Composition		Trinitrobenzoic acid identified at			
% H_2SO_4	% HNO_3	98-100°C	93-96°C	87-93°C	85-90°C
81.5	15.0	in 15 hrs.	in 2 hrs.	in 3.5 hrs.	nil at 5 hrs.
84.0	10.0	-	" 3.5 "	-	nil at 5 hrs., traces at end of 7 hrs.
88.0	6.0	-	" 3.5 "	-	nil at 7 hrs.

These nitroaldehydes are unbelievably stable towards mixed acid below 85°C. Above this temperature, however, some mechanism must be responsible for the retardation of the oxidation of trinitrobenzaldehyde. The nitrobody phase suggested itself as a likely means of protection and the following experiments (table 18) indicate work along this line.

Experiment 5 could not be duplicated. On repeating the experiment only trinitrobenzoic acid was isolated. This phenomenon has occurred on one previous occasion under similar conditions and serves to emphasise the narrow demarkation line existing between the formation of "A" and trinitrobenzoic acid.

The effect of 2:4-D.N.T. (expts. 9 and 10) is noteworthy /

noteworthy and is probably accounted for by the greater affinity of D.N.T. for HNO_3.

Experiment 5 was repeated (a) varying the rate of agitation with the addition of a trace of (b) NO_2 but all gave rise to trinitrobenzoic acid.

TABLE 18. EFFECT OF NITROBODY ON STABILITY OF TRINITROBENZALDEHYDE.

Expt No.	Nitrobody gms.	Trinitro-aldehyde gms.	Time hrs.	Acid cc. **	Product insoluble in carbon tetrachloride m.pt. °C
1	3 gm. T.N.T.	0.5	13	2.5	nil
2	3 gm. "	0.5	13	5.0	trace.
3	6 gm. "	0.5	17	7.5	nil
4.	6 gm. "	0.5	17	10.0	trace.
5	6 gm. "	0.5	7	12.5	270°C(d.)-"A"
6	6 gm. "	0.5	7	15.0	220°C(d.)-T.N.B.A.
7	6 gm. "	0.5	7	20.0	220°C(d.)-T.N.B.A.
8	6 gm. "	0.25	7	15.0	nil
9	6 gm. 2:4-D.N.T	0.5	7	15.0	nil
10	6 gm. "	0.5	7	20.0	nil

** Acid composition = 84% H_2SO_4, 10% HNO_3, 6.0% H_2O

Using acids of composition 88% H_2SO_4, 6% HNO_3, 6% H_2O and 75% H_2SO_4, 15% HNO_3, 10% H_2O under conditions akin to those existing in table 18 resulted in trinitrobenzoic acid formation again. Similarly the effect of two phases was as follows: 10 gms. T.N.T. (pure) /

(pure) were heated for 100 hrs. at 100°C with 50 ml. mixed acids of composition below - table 19.

TABLE 19.

	(1)	(2)
Acid Composition % H_2SO_4	84.0	75.0
% HNO_3	10.0	17.0
% H_2O	6.0	8.0
Number of phases	2	1
% insoluble in CCl_4	4.1	12.13
m.pt. insoluble material °C	235	230
Decarboxylated product m.pt. °C.	115-8	115-8

Again only trinitrobenzoic acid resulted.

Since the presence of nitrobody does not explain the formation of "A", attention was focussed on the isomerisation of o-nitroaldehydes.

ISOMERISATION.

Shultz and Ganguly (Ber. 1925,58,702) state that 2:4-D.N.T. is stable to light. On the other hand, 2:6-D.N.T. by exposure to light is converted into a yellow substance, probably 2:6-dinitroso-4-hydroxy benzyl alcohol and a dark yellow substance. Exposure of 2:4:6-T.N.T. to bright sunlight for three months caused the setting point to fall from 80 to 74°C.

By examining this last reaction, they found that the action of light in an atmosphere of oxygen, hydrogen, nitrogen or under vacuum led to the production of two tautomeric substances neither of which melt below 280°C and are considered to be 2-nitro-6-nitroso-

nitroso-5-oxy methyl-p-benzoquinone-4-oxime and 2-nitro -4-nitroso-5-oxy methyl-o-benzoquinone-2-oxime (fig. 14 K). Structure H (fig. 14) is assumed to be the precursor of the above products. The physical properties of these tautomeric substances, however, indicate that they are not by-product "A" - e.g. both are red in colour but the para quinone is readily soluble in cold acetone and water, whereas the ortho quinone is practically insoluble. Moreover, both compounds, on boiling five minutes with acetic anhydride and anhydrous acetate, yield the same 4-nitro-2:6-dinitroso-3-acetoxy benzyl acetate - a reaction which "A does not undergo.

In 1901 Ciamician and Silber (Ber. 1901,34, 2040) did work on o-nitroaldehydes and showed that in acetone, ether or benzene solution, isomerisation to the nitroso benzoic acid occurs. In alcoholic solution they found that the ester of the nitrobenzoic acid was formed.

The fact that di- and tri-nitrobenzaldehydes gave precipitates with phenyl hydrazine hydrochloride and semicarbazide suggested that these compounds behaved also as aldehydes but there was a possibility that the linkage was through the nitroso rather than the aldehydic group. Accordingly, the phenylhydrazone of 2:4-dinitrobenzaldehyde was prepared, recrystallised from /

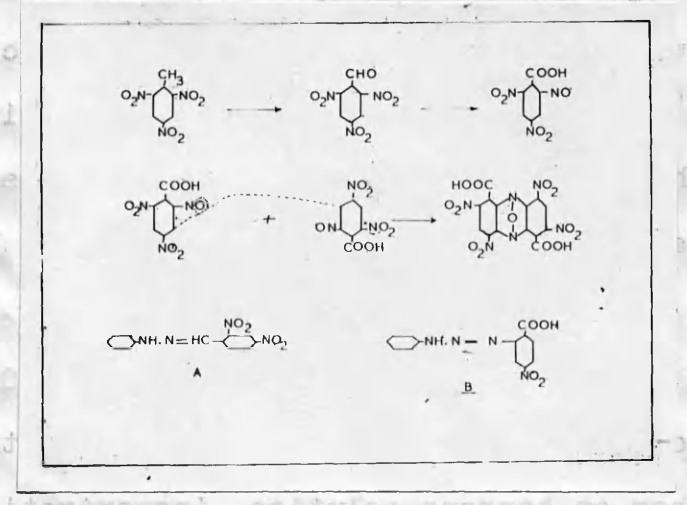


FIG. 15.

from alcohol and the nitro group determined by $TiCl_3$. The experiment indicated that 11 hydrogens were required for reduction, which is intermediate between structures A and B (fig. 15). 12 hydrogens would be required by structure A if only nitro groups were reduced and 10 hydrogens would be required for structure B if the nitro group was reduced and the double bond ruptured. The result obtained indicated a possible dynamic equilibrium between nitroaldehyde and nitroso acid formation. However, since the stability of double bonds towards $TiCl_3$ was in doubt, this portion of the work was suspended for more direct evidence.

The theory now envisaged was that T.N.T. was oxidised to the aldehyde which isomerised to the 4:6-dinitro-2-nitroso benzoic acid which was stable towards mixed acid. In the presence of concentrated sulphuric acid condensation ensued (fig. 15). Alternatively, the trinitrobenzaldehyde condensed with nitrous acid or some such compound occurring naturally in the spent acid to give a product stable to mixed acid. Under the influence of sulphuric acid, elimination followed by condensation would ensue.

2-Nitroso-4:6-dinitrobenzoic acid was first prepared by Sachs and Everding (Ber. 1902,35,1236; 1903, 36,960) by the action of daylight (3 weeks in benzene solution) /

solution) on 2:4:6-trinitrobenzaldehyde. It is described in the literature as a brown precipitate, m.pt. 229°C (d.) which crystallises from benzene with one molecule of solvent of crystallisation. Secarneau and Lupas (Bull.Soc.Chim. 1936,(v),3,1161) record its isolation from 2:4:6-trinitrobenzaldehyde by exposure to daylight for two weeks in benzene solution and describe it as a brown precipitate m.pt. 229°C (d.).

Attempts have been made to reproduce these results by irradiation of benzene solution of trinitro benzaldehyde with ultraviolet light. In earlier experiments, using specimens of trinitrobenzaldehyde of moderate purity, brown products separated from the reaction mixture after comparatively brief periods of irradiation. Considerable decomposition, however, also occurred. When aldehyde of high purity was employed, solid material was deposited at a very much slower rate, and in the place of brown precipitates, yellow microcrystalline material was obtained. Several experiments were performed, and the shades of the various specimens isolated varied slightly in colour (perhaps due to physical state), but melting points were fairly consistent (ca. 200 - 205°C).

IRRADIATION OF 2:4:6-TRINITROBENZALDEHYDE.

7 gms. 2:4:6-trinitrobenzaldehyde (prepared as on p.146), dissolved in 200 cc. moist benzene in a quartz /

quartz flask, fitted with a reflux condenser, were irradiated (U.V. light) for forty hours. At the end of every ten hours, the solid matter which separated was thoroughly removed from the sides of the flask and collected and the mother liquor returned to the flask for further irradiation. At the end of forty hours the mother liquor was separated and approximately 3 gms. aldehyde recovered therefrom. The various samples of irradiated product were extracted with boiling benzene and dried.

Several irradiations were carried out and products melting at 205-210°C (d.), 205-208°C (d.), 200-205°C (d.) were obtained. The microscopic yellow needleshaped prisms were sparingly soluble in ether, chloroform and toluene, soluble in glacial acetic acid, readily soluble in alcohol, acetone and methyl-ethyl ketone. Attempts at crystallisation failed. After drying in a vacuum desiccator over sulphuric acid the analysis found was C 46.2, H 2.95, N 13.4%. The nitroso acid - $C_7H_3N_3O_7$, requires C 34.8, H 1.24, N 17.4%. The nitroso acid with one molecule of benzene of crystallisation - $C_7H_3N_3O_7,C_6H_6$ - requires

C 48.9, H 2.8, N 13.16%

SALTS OF IRRADIATED PRODUCT.

The /

The irradiated compound is acidic in character - an ethereal extract gave a precipitate with a few drops of pyridine, piperidine or quinoline. The piperidine and pyridine salts were less easily prepared than the quinoline salt owing to their extreme solubility.

QUINOLINE SALT. The irradiation product was dissolved in alcohol, and excess of quinoline added. The salt was collected and washed with alcohol, purified by dissolving in absolute alcohol and allowing to separate out. A reddish brown amorphous powder was obtained m.pt. 147-8°C.

If the irradiation experiment were performed in quinoline solution, it was to be expected that greater yields of the quinoline salt of 4:6-dinitro--2-nitroso benzoic acid would be obtained. Accordingly, a number of experiments were carried out using benzene and toluene admixed with quinoline, also with quinoline alone, and irradiating for varying periods of 10 to 80 hours. Except for the quinoline solution, these resulted in recovery of unchanged aldehyde. With quinoline, a small amount of a light brown solid separated which, after purification from alcohol, gave m.pt. 154-8°C.

Dioxan and Dioxan + quinoline solutions were tried /

tried with no better results. The effect of an alcoholic nitrous acid solution on the aldehyde in the absence of ultra violet light was also investigated but no product ressembling the nitroso acid was isolated.

That the reactions suggested in fig. 15 p. 113 could proceed along such lines was shown by the fact that the compound m.pt. 205°C (d.) isolated by irradiation of a benzene solution of 2:4:6-trinitro benzaldehyde gave by-product "A" on heating with concentrated sulphuric acid at 100°C for 4 hrs.

Attempts were therefore made to isolate 4:6--dinitro-2-nitroso benzoic acid after heating the aldehyde with concentrated sulphuric acid. 0.5 gm. aldehyde was heated with 5 cc. 94% H_2SO_4 for 5 hrs. At the end of this period, by-product "A" separated and only aldehyde could be detected in solution. The experiment was repeated using 85% H_2SO_4 with similar results.

CONCLUSIONS.

In this chapter, trinitrobenzaldehyde was shown to be less stable than dinitrobenzaldehyde towards 85% H_2SO_4 at 100°C and that by-product "A" was formed as a result of the interaction between trinitro benzaldehyde and H_2SO_4. Towards mixed acid, trinitro benzaldehyde was shown to be more stable than dinitro benzaldehyde and that at temperatures below 85°C they were unbelievably stable. The oxidation of these aldehydes /

aldehydes, moreover, was inhibited by the presence of nitrobody especially 2:4-D.N.T. In all cases, however, using mixed acid trinitrobenzoic acid rather than by-product "A" formation resulted.

The mechanism of by-product "A" formation is not yet conclusive but there is no doubt that it is akin to the scheme outlined in fig. 15 p. 113. The only link missing in this chain is the isolation of the nitroso acid from trinitration and renitration slurries.

By-product "A" has no doubt the structure suggested by B or C fig. 14 p. 104 but conclusive proof will be required from spectrographic and/or X-ray analysis.

CHAPTER 16.

DINITRO CRESOLS AND DINITRO BENZOIC ACID.

By-product "A" (p. 84) has been isolated from the renitration of alpha T.N.T. Trinitrobenzoic acid may also be formed (p. 86). So far no mention has been made of dinitro cresols and dinitro benzoic acids.

Dinitrocresols have been isolated from M.N.T. in the batch nitration of toluene, and occur to the extent of about 0.3% but there is no record of their presence in mono- to tri-nitration. This chapter deals with the estimation and distribution of the dinitro cresols and dinitrobenzoic acid in the nitration of M.N.T.

At the completion of a nitration of M.N.T. (p. 80) without washing and drying at the dinitro stage the nitrobody and spent acid were treated as follows.

ACID SAMPLES.

A known weight of the acid sample was drowned in 400 cc. water and after cooling, the nitrobody was filtered off. The acid layer was then extracted with ether until the ether showed no colour, a process involving some four extractions. The ether extract was added to the filtered nitrobody for that sample and the whole was evaporated nearly to dryness. The

sample /

sample was taken up in 500 cc. chloroform and any by-product "A" filtered and discarded.

NITROBODY SAMPLES.

100 gms. nitrobody were dissolved in 500 cc. chloroform and by-product "A" filtered as before.

TREATMENT OF THE CHLOROFORM SOLUTIONS.

The solutions were agitated with saturated sodium carbonate solution. Four washes were carried out on each sample, the sodium carbonate extract being washed twice with chloroform to remove adhering nitrobody, acidified with hydrochloric acid and extracted four times with ether. The ether solution was evaporated until about 25 cc. remained and this was transferred to a tared 100 cc. beaker, evaporated to dryness and weighed. Some dried samples, especially those obtained from the T.N.T. part of the process, did not crystallise but remained as a syrupy mass. Previous tests showed the necessity for treating the samples in as short a time as possible to avoid long contact with alkali. In the tests carried out, all samples were extracted with sodium carbonate, acidified and ether extracted on the day of sampling.

ESTIMATION.

In order to determine the proportion of nitrocresols to other acidic bodies, two estimations were carried out /

were carried out, the extracted nitrobody being sub-divided for that purpose.

METHOD I. This consisted of titrating with N/10 NaOH using fluorescent indicators in ultra violet light. Umbelliferone, quinine sulphate, acridine and o-coumaric acid were examined, the latter two being the more satisfactory for this purpose. Moreover, it was found that the acridine end point corresponds to the neutralisation of dinitrobenzoic acid, whereas the o-coumaric acid end-point occurred when both nitro cresol and dinitrobenzoic acid had been neutralised (see table below). In the presence of nitrobody these end points were sometimes difficult to determine, but they gave some indication of the proportions present.

	cc. 1.2 N/10 NaOH	
Indicator	0.2gm. dinitrocresol	0.2gm. dinitrobenz.
o-coumaric acid	9.0cc. = 0.214 gm.	8.4cc. = 0.213 gm.
Acridine	no end point	8.4cc. = 0.213 gm.

METHOD 2. This consisted of acetylating the nitro cresols. It was found, in preliminary experiments with known weights of dinitrocresols and dinitrobenzoic acid, that a yield of acetylated product greater than 95% was obtained when 1 gm. total nitrobody was treated with acetic anhydride containing a few drops of phosphoric acid for 1 hr. at 90 to 100°C. The acetyl derivative

was /

was recovered by diluting the solution and boiling a few minutes to dissolve the dinitrobenzoic acid. On cooling, the acetyl derivative of 3:5-dinitro-p-cresol was precipitated and could be filtered into a tared sinter glass crucible. The product was given one wash, dried and weighed.

Dinitro Cresol gms.	dinitro benzoic acid gms.	Time hrs.	Acetic anhydride cc.	Wt. of ppt. recovered	% of theory.
1.0	-	2	25	1.14	95.5
1.0	-	3	25	1.18	97.4
1.0	-	1	12.5	1.16	96.5
0.5	0.5	1	12.5	0.60	99.3

On acetylation of extracts from nitration slurries, no products were obtained.

It was thought possible that in the extraction by chloroform the dinitrobenzoic acid might remain in the insoluble portion along with by-product "A". Experiments, showed that the solubility at 18°C was 0.775 gm. 2:4-dinitrobenzoic acid per 100 cc. solvent. Since approximately 500 cc. chloroform were used to dissolve the samples and at temperatures about 40°C, it is presumed that all the dinitrobenzoic acid was dissolved. Results are tabulated overleaf.

A difference in titrations with acridine and o-coumaric acid existed. Since no acetylated products were /

were found, indicating the absence of nitrocresols, the difference in the titre can only be attributed to the presence of other acidic nitrobodies. As the amounts of the latter were small, they were not investigated further at this stage.

	Acid	Nitrobody (T.N.T.)
Wt. recovered by ether extraction of acidified sodium carbonate extract (W) gms.	2.67	2.12
Wt. used for NaOH titrations (W_1) gms.	0.92	1.18
Titre using 1.2 N NaOH (a) acridine end point (b) o-coumaric acid	36.0 37.0	48.0 57.0
Dinitrobenzoic acid for W gms. extract i.e. for 300 gms. acid or 100 gms. nitrobody - gms.	2.66	2.21

Taking the acridine end-point as a measure of 2:4-dinitrobenzoic acid, it can be seen from the above figures that the weight of dinitrobenzoic acid obtained by calculation approaches closely the total weight of extracted nitrobody. This would appear to justify the assumption that the substance was indeed dinitrobenzoic acid or an acidic body of approximately the same molecular weight.

4 kilos T.N.T. spent acid were accumulated and extracted as before, yielding 6 gms. purified acidic nitrobody /

nitrobody which then crystallised from alcohol gave a white product m.pt. 174-5°C. This, on titration with N/10 NaOH, proved to be 98% pure 2:4-dinitrobenzoic acid, as was confirmed by a mixed melting point.

It was deemed advisable at this stage to determine the stability of dinitrobenzoic acid and 3:5-dinitro-o- and p-cresols towards mixed acids. Accordingly, tests were carried out with acids of the following concentrations.

No.	1	2	3	4	5	6	7
% H_2SO_4	75.0	74.0	69.0	86.0	78.6	80.0	93.0
% HNO_3	-	13.6	17.4	6.2	5.0	1.0	-
% H_2O	25.0	12.4	13.6	7.8	16.4	19.0	7.0

0.5 gm. dinitrocresol or dinitrobenzoic acid was added to 100 gms. of the above acids and heated to 90°C with occasional shaking. From all the above acids, dinitro benzoic acid was recovered unchanged after one hour's contact. Both o- and p-dinitrocresols, however, dissolved to give yellow solutions which decomposed rapidly with gas evolution. Reaction started at 30 to 40°C and in less than 15 mins. acids 2 to 5 were colourless. With acid 6, the time taken for decolourisation was two hours. With acids 1 and 7, practically all the dinitrocresol was recovered unchanged, but in all other cases only a small amount of an /

of an oxidation product was isolated. This melted 99-104°C and on recrystallising from alcohol gave a small quantity of crystalline product, insoluble in chloroform with the same melting point, which burned with a non-smoky flame and was apparently oxalic acid.

The above tests showed that whereas dinitro benzoic acid was stable to mixed acids, dinitrocresols were decomposed immediately they came into contact with nitric acid.

So far it has been shown that dinitrobenzoic acid is present in the spent acid from trinitration but it was assumed in all other cases that extracted nitrobody was dinitrobenzoic acid because of its equivalence on titration with alkali. Consequently a sample of crude T.N.T. was taken and treated as before (p.120)

Crude T.N.T. No.	% recovered by ether extract. of acidified Na_2CO_3	Vol, of 1.248 N/10 NaOH acridine end point ccs.	% acid, as dinitro-benzoic acid.
1	1.62	49.0	1.30
2	1.58	57.0	1.51
3	1.33	47.0	1.25

In an attempt to prove the presence of dinitrobenzoic acid in the above samples, a kilo sample was taken and treated as above. A red jelly like mass resulted after evaporating off the ether. This was steam /

steam distilled but no product was extractable from the distillate. Sovents - alcohol, petroleum ether (b.pt. 60-80°C), dioxan, acetone, benzene, glacial acetic acid, formic acid, concentrated H_2SO_4, 70% HNO_3, pyridine, alkali-acid, M.N.T., - were tried but none gave a crystalline substance. A lead salt was prepared by the addition of lead acetate to an alcoholic solution of the jelly. This salt was yellow in colour and exploded violently at 286°C. The corresponding salt from 2:4-dinitrobenzoic acid had a pale yellow colour and did not melt below 360°C. The yellow salt of the unknown acidic body was decomposed with dilute HNO_3 and on cooling a small amount of a brown material was isolated which did not melt below 360°C.

Alpha, beta and gamma T.N.Ts. were dissolved in chloroform and treated with alkali as above to ascertain if any similar viscous body could be isolated. No organic product, however, remained after acidifying and extracting the solution with ether.

Alternative methods of extraction of the acidic bodies from crude T.N.T., avoiding the use of large volumes of chloroform, were now investigated from a qualitative view point. (a) Crude molten T.N.T. was pelleted in water, melted and stirred with hot saturated /

TABLE 20 . ACIDIC PRODUCTS OBTAINED BY BICARBONATE EXTRACTION OF CRUDE T.N.T.

$NaHCO_3$ extract acidified.

Product separating
treated with chloroform

insoluble m.pt. 215°C
semi decarboxylated
by-product A.

Soluble. crystallised
from 70% HNO_3 m.pt.
182-5°C, recrystallised
from toluene m.pt. 195°
No Sulphur in compound.

Ether extract evaporated
treated with chloroform

Insoluble. Boiled
30 mins. with water,
fractional cooling

Compound, m.pt. 120°C
Naphthalene addition
compound m.pt. 150°C
- Trinitrobenzene.

red jelly crystallised
from toluene m.pt.
217°C (d.)
By-product A.

Soluble. A red
jelly, no sulphur
in compound.
completely soluble
in 70% HNO_3 - no
compound separated
on cooling.

saturated sodium carbonate solution. The resulting solution was cooled and any nitrobody separating filtered, the filtrate being acidified. A dark brown sticky mass separated while ether extraction of the solution gave a black jelly. (b) Crude molten T.N.T. was pelleted in cold saturated carbonate solution. After filtering, the solution was cooled, refiltered and acidified to give a small amount of black material. Ether extraction of the filtrate gave a jelly akin to that in (a). The above two methods were failures probably because of the alkalinity of the extract. (c) Crude molten T.N.T. was stirred with sodium bicarbonate solution at 85°C. The extract was orange red in colour and on acidification gave a light yellow coloured product which was filtered off. The filtrate was extracted with ether, which on evaporation yielded a similar product. This was treated according to the following scheme (table 20).

The amount of product obtained was very small, trinitrobenzene being of the order of 0.005%. The result of these tests was to show that extraction of crude molten nitrobody by hot alkali results in the decarboxylation of such compounds as trinitrobenzoic acid and by-product "A".

The rate of decarboxylation of trinitrobenzoic acid /

acid was estimated by the weight of trinitrobenzene separating on cooling after boiling for definite time intervals. This rate was found to be the same in water, dilute ammonia and 2N Na_2CO_3. Incidentally, this offered a method of estimating trinitrobenzoic acid in the presence of by-product "A". 0.5 gm. by-product "A" + 0.5 gm. trinitrobenzoic acid was added to 250 cc. water containing 1 cc. ammonia (S.G. 0.88) and the mixture refluxed for 30 mins. On cooling the solution, trinitrobenzene separated and any remaining in solution was extracted with ether. During the refluxing, "A" is partially decarboxylated to the monocarboxylic acid (p. 99) which remains in solution as the ammonium salt. Evaporation to dryness of the remaining solution gave the ammonium salt m.pt. 238°C (d.). The disadvantage of the method was the destruction of the trinitro benzoic acid and the dicarboxylic acid form of "A", but the method, so far as it was investigated was quantitative.

It is possible that dinitrobenzoic acid may form low melting eutectics with D.N.T. or T.N.T. which may result in the formation of jelly like compounds. Dinitrobenzoic acid was added to alpha T.N.T. in successive small increments until the setting point reached a constant value. Table 21 gives the results obtained. /

obtained.

TABLE 21. SOLUBILITY OF 2:4-DINITROBENZOIC ACID IN ALPHA T.N.T.

	S.P. °C
S.P. alpha T.N.T.	79.88
" " " + 0.74% D.N.B.A.	78.50
" " " + 1.25% "	79.21
" " " + 1.96% "	78.90
" " " + 2.92% "	78.51
" " " + 3.90% "	78.06
" " " + 5.04% "	77.53
" " " + 6.06% "	77.18
" " " + 6.72% "	77.13
" " " + 7.74% "	77.10

On pouring the molten mixture into excess carbon tetrachloride the dinitrobenzoic acid was recovered unchanged. It will be observed that the solubility of 2:4-D.N.B.A. in alpha T.N.T. is of the order of 6% and that the fall in set point follows approximately Raoult's law.

Table 22 summarises the results when 2:4-D.N.T. was used in place of alpha T.N.T. It will be observed from this table that the solubility of D.N.B.A. in 2:4-D.N.T. is slightly higher than in the above case, being 7.4% and in this case Raoult's law holds.

Thus, /

Thus, although 2:4-dinitrobenzoic acid has been identified in the spent acid, the acidic body present in the nitrobody phase can only be assumed to be 2:4-dinitrobenzoic acid because of its equivalence on titration with alkali.

TABLE 22. SOLUBILITY OF 2:4-DINITROBENZOIC ACID IN 2:4-D.N.T.

	S.P. °C.
S.P. 2:4-D.N.T.	69.70
" " " + 0.58% D.N.B.A.	69.45
" " " + 1.32% "	69.10
" " " + 3.10% "	68.40
" " " + 3.98% "	68.00
" " " + 5.16% "	67.50
" " " + 6.32% "	67.00
" " " + 7.40% "	66.60
" " " + 8.12% "	66.60

Schmitt (Mem. Poudres, 1937,27,131) has isolated a compound 2:4-dinitro-5-hydroxybenzoic acid m.pt. 188°C from crude T.N.T. but the presence of this compound could not be proved e.g. by acidification of the lead salt. Moreover, the equivalent molecular weight of the hydroxybenzoic acid is 114 but with the fluorescent indicators used, 228 is possible.

The final conclusion, therefore is that

(a) 0.9% of the spent acid is dinitrobenzoic acid.
(b) 1.5 to 2.0% of the crude T.N.T. is acidic possessing a molecular weight or equivalent of 212.

E X P E R I M E N T A L

S E C T I O N.

PART II.

REMOVAL OF NON ACIDIC BY-PRODUCTS:

PURIFICATION OF CRUDE T.N.T.

CHAPTER 17.

LOSS ON SULPHITING T.N.T.

T.N.T. produced by nitration is impure, containing unsymmetrical T.N.Ts. and nitrocarboxylic acids. Little can be done to prevent oxidation losses and as acidic impurities are to some extent removed by hot water washing they may be neglected in this section.

The unsymmetrical T.N.Ts. still remain, however, and it is their removal together with the mechanism of the reaction that is investigated in this section.

Chapter 6 deals with the action of sulphite on T.N.Ts. There, it is shown that sulphite primarily removes the unsymmetrical T.N.Ts. and of course any acidic foreign bodies. Moreover a secondary reaction occurs, though not so readily, between alpha T.N.T. and sulphite (Ministry of Munitions, Tech. Records No. 2, p. 85).

The sulphite liquor used in the following experiments has the composition 4% crystalline sulphite ($7\ H_2O$), 0.8% boric acid. The pH of sodium sulphite is 9.3 - 9.8 whereas that of the boric acid - sulphite solution is 7.6 - 8.0 depending on the purity of the reagents. Sulphiting is carried out at 80°C until the /

TABLE 23.

	% H_2SO_4	°C	
		Wet S.P.	Dry S.P.
Acid T.N.T.	5.5		77.4
After collection in water	4.1	75.3	-
After 1st. water wash	2.1	73.4	-
" 2nd. " "	0.6	74.0	-
" 3rd. " "	0.3	74.2	-
" 4th. " "	0.1	73.2	-
" 5th. " "	0.1	72.8	77.8
	pH		
After 1st. sulphiting	7.5	76.1	78.9
" 2nd. "	8.5	76.8	-
" 1st. water wash	8.1	-	-
" final water wash	-	76.8	80.0

TABLE 24.

Original wt. of washed, dried crude T.N.T. 100 gms.

S.P. °C 77.47°C

	Sample 1	Sample 2
After 3 sulphite + 3 water washes Wt. dry T.N.T.	92.3	92.1 gms.
Loss of T.N.T.	7.7	7.9 gms.
S.P. of T.N.T. °C	79.86	79.94
After 2 more sulphite + 3 water washes - Wt. dry T.N.T.	87.2	86.9 gms.
Total loss of T.N.T.	12.8	13.1 gms.
Final dry S.Ps.	79.46	79.73

the final wet S.P., after washing, is greater than 76.5°C which is equal to a dry S.P. of 80.15 to 80.2°C (p. 81).

A large number of tests were carried out to determine the total loss involved in sulphiting and washing crude T.N.T. as follows: The crude T.N.T. was washed with hot water until free from mineral acid, dried and the S.P. taken (see table 23). 100 gms. samples of this crude dry T.N.T. were given three sulphite washes (100 cc. each of the above composition) at 80°C, each wash lasting 30 mins. Three water washes, each of 30 mins. duration followed. Table 24 summarises the results.

From this data it can be observed that neglecting the preliminary washing of the crude T.N.T. the average loss for one sulphite wash followed by hot water washing is 2.5%. Of this, the loss due to water washing is approximately 0.2% (from solubility data). The remaining loss of 2.3% is composed mainly of unsymmetrical T.N.Ts. but also includes a loss of alpha T.N.T. The D.N.T. content (2:4- and 2:6-) and the unsymmetrical T.N.Ts. can be calculated if the crude T.N.T. be sulphited to maximum S.P. (p. 135). The D.N.T. content is (80.8 - final dry S.P.) x 1.67 % and /

and the unsymmetrical T.N.Ts. are estimated from fig. 13 p.81.

The effect of boric acid is well illustrated in the following experiment -conditions as described earlier except that each sulphite wash lasted 20 mins. and each water wash 15 mins.

TABLE 24. EFFECT OF BORIC ACID ON THE LOSS OF T.N.T.

Expt. No.	Solution	pH	pH after 1st.	2nd.	3rd. sulph.
1 - 6	4% $Na_2SO_3,7H_2O$ 0.8% H_3BO_3	7.8	7.6 - 8.2	8.6	8.8
7-10	4% $Na_2SO_3,7H_2O$	9.3	9.3	10.46	10.3

TABLE 24 contd.

Expt. No.	Dry S.P. °C of crude	Purified T.N.T.	% loss on crude T.N.T.
1 - 6	76.8	78.65	4.1
7 - 10	76.8	78.85	6.75

It will be noted that the loss is much higher with unbuffered sulphite though S.P. is slightly higher than for buffered sulphite. For minimum loss, therefore, the pH of the solution should be as close to 8 as possible. In addition to minimising the loss it has also the advantage in preserving the colour of the final T.N.T.

CHAPTER 18.

THE SULPHITING OF T.N.T. - D.N.T. MIXTURES.

It is easy to visualise a T.N.T. containing traces of D.N.T. This will lower the S.P. of the final purified T.N.T. and if sufficient D.N.T. be present may render it unfit for commercial purposes. Consequently it is necessary to know whether sulphiting will successfully remove D.N.T.

Data on the effect of sulphiting 2:4-D.N.T. was conflicting. Mécir (Chim. et Ind. 1933,29, special no. p. 952) states that though the action of sulphite on the unsymmetrical D.N.Ts. in the cold is very slight, at temperatures greater than 50°C, chemical reaction commences. On the other hand, with 2:4-D.N.T. he states that it does not react to any great extent even at elevated temperatures though some reaction takes place above 70°C. Accordingly, experiments were conducted on sulphiting T.N.T. - D.N.T. mixtures at 80°C, the S.P. of the T.N.T. chosen being comparable with the purest commercial product.

50 gms. recrystallised alpha T.N.T. (S.P. 80.46°C) were mixed with 1 gm. 2:4-D.N.T. (m.pt. 69 to 69.5°C) giving a 1.96% mixture of D.N.T. and the S.P. determined. The mixture was sulphited with 50 cc. (measured hot) sulphite liquor of composition 4% crystalline /

crystalline sulphite, 0.8% boric acid at 80°C for 20 mins. After separation of the waste sulphite liquor the mixture received four separate water washes at 80 to 85°C, each lasting 5 mins. Finally, after drying for four hours on a boiling water bath, the S.P. was determined in duplicate. This procedure was repeated three times.

Dry S.P. of alpha T.N.T.	Dry S.P. of T.N.T.-D.N.T. mixture			
	before sulphiting	after sulphiting		
		1st. wash	2nd. wash	3rd. wash
80.46°C	79.37°C	79.54	79.46	79.41°C

The increase in S.P. of 0.17° after first sulphite wash is explained by the presence of unsymmetrical T.N.Ts. in the original T.N.T. This was confirmed by sulphiting the original T.N.T. (S.P. 80.46°C) with 50 cc. sulphite at 80°C for 10 mins. The increase by this treatment was 0.16°C.

The gradual decrease in S.P. as sulphiting proceeds may be due to (a) the removal of alpha T.N.T. in preference to D.N.T. or (b) decomposition or possibly both.

If D.N.T. be removed preferentially to T.N.T. in the hot water washing rather than in the sulphiting, it should be possible to detect it by lowering of the melting point of the nitrobody separating from the washings, including the hot sulphite wash. The melting point /

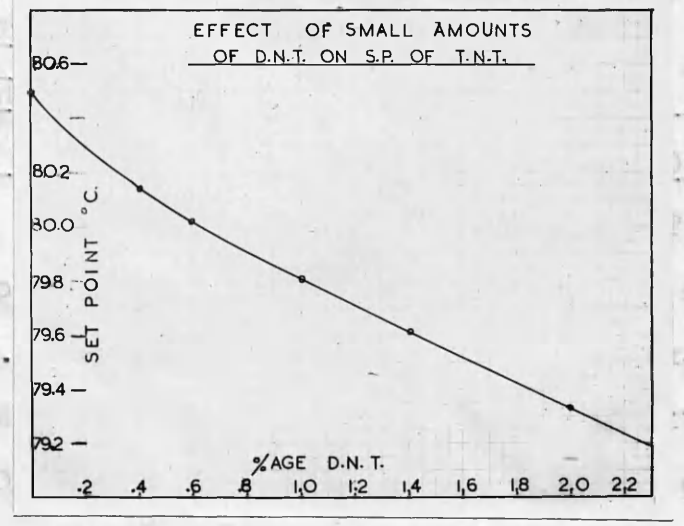

EFFECT OF SMALL AMOUNTS
OF D.N.T. ON S.P. OF T.N.T.
SET POINT °C.
80.6
80.2
80.0
79.8
79.6
79.4
79.2
%AGE D.N.T.
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2

FIG. 16

point of all specimens, however, was 78 to 79.5°C indicating that 2:4-D.N.T. was not removed preferentially to T.N.T.

Since hot sulphiting and hot water washing had little or no effect on the S.P. of a T.N.T. - D.N.T. mixture, it is thus possible to determine the approximate percentage of 2:4-D.N.T. in T.N.T. by sulphiting to remove isomers and determining the final S.P. Although curves existed (p. 174) showing the effect of D.N.T. on the S.P. of alpha T.N.T. the lowest percentage D.N.T. taken was about 5% - a figure not likely to occur in crude T.N.T. S.Ps. were therefore tabulated for a T.N.T., S.P. 80.49°C mixed with varying amounts of 2:4-D.N.T. up to 2% but the graph was curved towards the higher S.Ps. (fig. 16). For a T.N.T. of S.P. 80.8°C, however, a straight line was obtained, 1.67% 2:4-D.N.T. lowering the S.P. by 1°C.

It was considered probable that the unsymmetrical T.N.Ts. might form eutectics with 2:4-D.N.T. facilitating its removal. Consequently a synthetic "crude" T.N.T. was prepared and sulphited. If the unsymmetrical T.N.Ts. have no such effect a constant S.P. in the neighbourhood of 79.40°C should be obtained (cf. fig. 16)

50 gms. recrystallised T.N.T. (S.P. 80.47°C) together /

together with 2 gms beta T.N.T. (m.pt. 110-111°C), 1 gm. gamma T.N.T. (m.pt. 103°C), 1 gm. 2:4-D.N.T. were mixed and sulphited till no further rise in S.P. resulted

Mixture	Dry S.P.°C
T.N.T.	80.47
Alpha + Beta T.N.T.	78.68
" + " + Gamma T.N.T.	77.67
" + " + " T.N.Ts. + D.N.T.	76.36
After 1st. Sulphiting lasting 20 mins.	77.86
" 2nd. " " " "	78.76
" 3rd. " " " "	79.31
" 4th. " " " "	79.37
" 5th. " " " "	79.47
" 6th. " " " "	79.41

The results show a maximum S.P. of 79.47°C while on p. 135, in the absence of beta and gamma T.N.Ts. the maximum S.P. was 79.54°C. It should be emphasised that this synthetic mixture contains approximately 6% unsymmetricals - a figure well in excess of that of T.N.T. manufactured from M.N.T., containing 4% meta isomer.

Similar experiments were conducted on a commercial washed and dried T.N.T. to which 2% 2:4-D.N.T. was added. The following table indicated the results and calculation - (80.8 - 79.28) x 1.67 = 2.5% ± shows that the

The T.N.T, contains 2.5% D.N.T. or since 2% D.N.T. was added, the original crude T.N.T. contained 0.5% D.N.T.

	S.P. °C
Dry S.P. of crude T.N.T.	78.46
" " " " " + D.N.T.	77.16
Dry S.P. after 1st. sulphiting lasting 20 mins.	78.26
" " " 2Nd. " " " "	79.28
" " " 3rd. " " " "	79.28

It was observed in all these experiments, even after six sulphitings, that the T.N.T. was still of remarkably good colour. The presence of 2:4-D.N.T., therefore, apparently inhibits the action of alkali on alpha T.N.T.

2:6-D.N.T. (m.pt. 66°C) prepared by reduction of 2:4:6-T.N.T. by $(NH_4)_2S$ was found to give the same depression of S.P. as 2:4-D.N.T. (i.e. 1.67% lowers the S.P. 1°C). Moreover 2:6-D.N.T., like 2:4- was not removed by sulphiting so that sulphiting to maximum S.P. gives 2:4 + 2:6-D.N.T. content of the final T.N.T.

CHAPTER 19.

MECHANISM OF SULPHITING.

Chapter 6 deals with the theory of sulphiting. There, it was shown that the main action of sulphite is to react with the unsymmetrical T.N.Ts. removing them as soluble sodium sulphonates by virtue of the replacement of a labile nitro group by the sulphonic acid group. However, alpha T.N.T. is also attacked by sulphite so much so that to cut the loss of alpha T.N.T. the solution must be buffered (p. 133).

There is no doubt that the reaction between sulphite and the unsymmetrical T.N.Ts. is as given above but at 80°C other side reactions occur as shown by the colour changes undergone by beta and gamma T.N.Ts. In the case of alpha T.N.T. the side reaction shown by beta and gamma T.N.T. becomes the predominant feature. No substitution of a sulphonic acid group for a nitro group is apparent here. Since the use of buffered in place of unbuffered sulphite lowers the loss of alpha T.N.T. it was justly thought that the action of sulphite on alpha T.N.T. was primarily due to the alkalinity of the solution. That this does not provide a complete solution is shown by the following experiment wherein 2% $NaNO_2$ (equivalent to 4% crystalline Na_2SO_3) is compared with a buffered sulphite solution of

composition /

composition 4% $Na_2SO_3,7H_2O$, 0.8% H_3BO_3. The sodium nitrite solution had pH = 8 whereas the buffered sulphite was 7.7. A known weight of pure recrystallised T.N.T. (S.P. 80.8°C) was given a nitrite treatment at 80°C followed by two hot water washes then dried for 3 hrs. The nitrite and water wash liquor were cooled, filtered, washed and the precipitate added to the main bulk of the T.N.T. A similar experiment was carried out with the buffered sulphite solution. The loss by sulphite action was four times greater than that by nitrite - the respective figures being 3.6 and 0.9%. Similar experiments carried out on a T.N.T. S.P. 80.2°C) gave losses, though smaller, of the same order viz. 1.44 and 0.37 respectively. Consequently the action of sulphite on alpha T.N.T. is primarily due to the sulphonic acid group probably along lines similar to the Piria reaction (p. 54).

Sulphite usage is further increased by reaction between sodium nitrite produced during the replacement of the nitro group by the sulphonic acid group and excess sulphite. This reaction is greatly affected by pH and has been investigated by various workers (Friend, Inorg. Chem., Vols. VI and VII; J.A.C.S. 1938, 60,(2), 1947; Chem Rev. 1940,26,49).

Thus during sulphiting three main reactions are proceeding /

proceeding

Na_2SO_3 + unsymmetrical T.N.Ts. = $C_7H_5N_2O_4.SO_3Na$ + $NaNO_2$.

Na_2SO_3 + $NaNO_2$ = ?

Na_2SO_3 + alpha T.N.T. = ?

Attempts were made to elucidate the mechanism of the action of sulphite on alpha T.N.T. Before proceeding to this feature, however, it was considered possible to recover the 4% unsymmetrical T.N.Ts. (present in the sulphite liquor as 2:4-dinitro-sodium-sulphonates) as 2:4-D.N.T. by pressure hydrolysis (H replacing SO_3H).

Steam distillation of the sulphite liquor before and after acidification with H_2SO_4 gave no volatile product. No product was extractable from the residue by the commoner organic solvents.

Hydrolysis under pressure was then attempted. 300 cc. sulphite liquor were acidified with 100 cc. syrupy phosphoric acid (Sp.G. 1.75). A small quantity of a red amorphous powder separated and was filtered off. 300 cc. filtrate were heated for 12 hrs. at 150°C in an iron bottle. A large amount of iron residue resulted and only a red jelly could be isolated from the filtrate. The use of the iron bottle was discontinued and glass screw stoppered bottles, tested to /

to 500 lbs./in^2 pressure were used. 300 cc. filtrate (as above) were placed in the bottle and heated to 150°C for periods up to 24 hrs. Difficulty was experienced in making the bottles perfectly tight, the rubber washers tending to perish especially for periods longer than 6 hrs. Chamois washers were tried with little advantage. After 1 hr. at 150°C a small quantity of a black amorphous solid was thrown out of solution m.pt. 195 - 200°C (d.). Extraction of the solution yielded only a red jelly.

Once on heating to 150°C for 12 hrs., due to the stopper leaking the liquid evaporated and a black residue remained behind. This was dissolved by means of acetone and after evaporation, an alcoholic extract of the mass gave a small amount of a white acidic substance which on recrystallisation from toluene had m.pt. 177-8°C. A mixed m.pt. with 2:4-dinitrobenzoic acid showed no depression and the product was concluded to be 2:4-dinitrobenzoic acid.

In order to eliminate the possible effects of SO_2, the filtered solution after acidification was boiled with 5 cc. bromine water, filtered and 300 cc. filtrate treated as above. Identical results were obtained. During one of those tests an explosion occurred, wrecking the oven. This showed that even when /

when acidified, unstable products were produced from sulphite liquors. It was therefore concluded that hydrolysis of the sulphonic acid group did not occur readily.

Reverting to the mechanism of sulphiting, the main line of attack was to react on alpha T.N.T. with sulphite under normal conditions and in an inert atmosphere and to try and isolate an identifiable product.

A large number of complicated products, chiefly resins and black amorphous compounds, were obtained which were difficult to analyse. The chief difficulty lay in obtaining them in a crystalline state for they were extremely soluble in water.

Various references existed in the literature as to the possibility of compounds like hexanitrodibenzyl being formed. Accordingly, a better line of attack was to prepare some standard products like trinitrobenzyl bromide and from that to prepare tetra- and hexa-nitrostilbenes and dibenzyls and see if they corresponded to any of the products obtained by the action of sulphite on alpha T.N.T.

THE NITROSTILBENES.

Literature.

Thiele and Escales (Ber. 1901,34,2342) recorded smooth /

smooth condensations of 2:4-D.N.T. with benzaldehyde, p-nitrobenzaldehyde and m-nitrobenzaldehyde giving 2:4-dinitrostilbene, 2:4:4'-trinitrostilbene and 2:4:3'-trinitrostilbene respectively. 80 to 95% yields were obtained by fusing equivalent quantities of nitrobody and aldehyde at 130 - 140°C in the presence of a little piperidine. In the case of o-nitrobenzaldehyde condensation was not so facile and the yield of 2:4:2'-trinitrostilbene was only 40%.

Ullman (Ber. 1908,41,2291) studied the condensation of 2:4:6-T.N.T. with aromatic aldehydes and by carrying out his condensations in alcoholic solution using piperidine as a catalyst he prepared 2:4:6-trinitrostilbene and 2:4:6:4'-tetranitrostilbene in good yield. Furthermore, Ullman claimed that the condensation of aromatic aldehydes with 2:4:6-T.N.T. proceeded more readily than those with 2:4-D.N.T., the methyl group presumably being activated by the additional nitro group in the ortho position.

Bishop and Brady (J.C.S. 1933,2367) repeated Ullman's work and substituted benzene for alcohol as the latter solvent gave rise to complex compounds. 2:4:6:3' and 2:4:6:2' tetranitrostilbenes were prepared from m- and o-nitrobenzaldehydes.

Strakosch (Ber. 1873,6,328) found that p-nitro benzyl /

benzyl chloride gave 4:4'-dinitrostilbene on treatment with KOH and similar stilbenes have been prepared by Ebbs (J.Prakt.Chem. 1845,34,340) and Bischoff (Ber. 1888,21,2072). Reich, Wetter and Widmer (Ber. 1910, 43,3060) state that 2:4:6-trinitrobenzyl bromide yields hexanitrostilbene when treated with alcoholic KOH but considerable decomposition occurs and the yield is poor. According to these authors, it crystallises from nitrobenzene in yellow needles m.pt. 211°C (d.).

Green and his co-workers (J.C.S, 1904,85,1424 and 1432; 1906,89,1602; 1907,91,2076) have studied the action of NaOH on the nitrotoluenes and have prepared 2:4:2':4'-tetranitrostilbene from 2:4-D.N.T. by treatment with sodium methylate in the presence of iodine (J.C.S. 1908,93,1721, see also p. 43). This method was unsuccessful, however, when applied to 2:4:6-T.N.T. for the preparation of hexanitrostilbene.

EXPERIMENTAL - Preparation of 2:4:6-Trinitrobenzaldehyde.

The preparation involves the condensation of T.N.T. and p-nitroso-dimethyl aniline. Sachs (Ber. 1902,35,1236; 1903,36,960), Lowy and Balz (J.A.C.S. 1921,43,341) made slight modifications in the method and claimed an improved yield of 60% and finally a yield of 80% was reported by Secarneau (Ber. 1931,64, 834 and 837). The methods of Sachs and of Lowy and Balz /

Balz were found unsatisfactory as both yielded an impure product and gave troublesome emulsions. Secarneau's method, however, overcame these difficulties.

180 gms. T.N.T. + 120 gms. p-nitroso dimethyl aniline + 4 gms. iodine in 400 cc. pyridine were intimately mixed. The mixture was kept thoroughly stirred, a cooling bath being applied when necessary. After 24 hrs. the product was collected and washed with acetone to give a yield of 200 gms. of the anil. 100 gms. of this anil were covered with excess HCl and warmed for 15 mins on the water bath. The reaction mixture was then cooled, allowed to stand 1 hr. and filtered. The aldehyde was washed first with concentrated HCl, then with dilute HCl and finally with H_2O. The yield was 50-55 gms. (80%). Crystallisation from alcohol gave colourless prisms m.pt. 119°C.

Preparation of Trinitrobenzyl Bromide.

The halogenation of 2:4:6-T.N.T. was first accomplished by Reich (Ber. 1912,45,804 and 3060). Subsequently, Ganguly (ber. 1925,58,708) improved the method and obtained a yield of 80%.

10 gms. T.N.T. + 5 cc. Br_2 + 3 gms. $MgCO_3$ were heated in a sealed tube for 16 hrs. at 150 - 160°C. The oily product was stirred with dilute HCl and repeatedly washed with water till free from bromine.

After /

After standing, with occasional scratching with a glass rod, the material was obtained in solid form. Crystallisation from alcohol gave small glistening plates m.pt. 63-5°C. Yield (crude) = 13 gms. (ca. 80%).

Attempts to Prepare 2:4:6 - 2':4':6'-hexanitrostilbene.

Some of the preparations of Thiele and Escales, Ullman, and Bishop and Brady (loc.cit.) were repeated and attempts were made to extend their methods to the synthesis of hexanitrostilbene from 2:4:6-T.N.T. and 2:4:6-trinitrobenzaldehyde but without success. No condensation occurred on fusing the reagents at 130 - 140°C or higher temperatures in presence of piperidine, and prolonged refluxing in benzene and alcohol solutions was ineffectual (expts. 1 - 5).

(1) 2.3 gms. T.N.T. + 2.4 gms. trinitrobenzaldehyde were dissolved in 90 cc. alcohol and 6 drops of piperidine added. The mixture was boiled under reflux for 6 hrs. but no condensation took place.

(2) similar to (1), but refluxing for 12 hrs. and piperidine added at the end of every four hours.

(3) 4.5 gms. T.N.T. + 4.8 gms. trinitrobenzaldehyde were fused together and 6 drops of piperidine added. The mixture was heated at 150 - 160°C for 5 hrs. but no condensation occurred.

(4) similar to (3), but temperature was maintained at 200°C /

200°C for 6 hrs. No condensation occurred.

(5) 11.5 gms. T.N.T. + 12.0 gms. trinitrobenzaldehyde were dissolved in 100 cc. benzene and 1 cc. piperidine added. The mixture was boiled under reflux for 40 hrs.. Condensation did not occur.

Unsuccessful attempts were made to reproduce the work of Reich, Wetter and Widmer (loc. cit.). Consistently low yields of a halogen free nitro compound were obtained. Purification was difficult, but after repeated crystallisation from nitrobenzene, the compound was eventually obtained as golden yellow, shining needles of indefinite melting point (darkened about 280°C, fused and decomposed about 300 - 320°C).

(6) 9 gms. 2:4:6-trinitrobenzyl bromide were dissolved in 100 cc. alcohol and efficiently agitated at 40°C. An alcoholic solution of KOH (1.7 gms. KOH in 50 cc. alcohol) was slowly run in over 3 hrs., stirring vigorously. After standing overnight, the product was collected, washed with alcohol and with water and crystallised repeatedly from nitrobenzene. As mentioned above glistening yellow needles were obtained. Found C 39.3, H 2.1, N 18.5%. Hexanitrostilbene requires C 37.35, H 1.3, N 18.7%. Moreover, literature records a melting point of 211°C (d.) for hexanitrostilbene as against the indefinite melting /

melting point recorded for the above substance.

The work of Green and his co-workers (loc. cit.) was readily reproduced and 2:4,2':4'-tetranitrostilbene was obtained in excellent yield. Attempts were then made to extend this method to the synthesis of hexanitrostilbene but these were unsuccessful. This failure appears to be due to the instability of T.N.T in presence of strong alkali. Accordingly, experiments were carried out using weaker bases but again without success (experiments 7 to 9). When excess of pyridine was employed, without the addition of another base a comples iodine compound was obtained, analysis being, C 22.3, H 2.2, N 9.7, I 51.5%.

(7) 25 gms. T.N.T. were dissolved in 60 cc. pyridine and a solution of iodine (32 gms.) in methyl alcohol (220 cc.) added. The mixture was agitated in a freezing mixture, and 70 cc. methyl alcoholic solution gradually run in and the whole allowed to stand overnight. Hexanitrostilbene could not be isolated from the reaction mixture.

(8) similar to (7) but lime was substituted for KOH. No condensation took place.

(9) 8 gms. 2:4:6-trinitrobenzaldehyde were dissolved in 50 cc. benzene (freshly distilled over phosphorus pentoxide/

pentoxide and 10 gms. trinitro benzyl bromide dissolved in 100 cc. dry benzene slowly added. When addition was complete, the mixture was refluxed for 24 hrs. taking suitable precautions to exclude moisture. The starting materials were recovered unchanged.

The nitration of trinitrostilbene was unsuccessful and Bishop and Brady (J.C.S. 1923,121,2367) report unfavourably on the preparation of stilbenes from azines. Reynold, Fuson and Cook (J.A.C.S. 1940,62,1180) describe stilbene derivatives prepared by the condensation of aromatic aldehydes and benzyl halides in the presence of zinc dust but the reaction with 2:4:6-trinitrobenzaldehyde and 2:4:6-trinitrobenzyl bromide was unsuccessful.

None of the products listed in the literature or examined were comparable with these obtained in the treatment of sulphite liquors. A list of these compounds follows.

2:4-dinitrostilbene - light yellow, m.pt. 139 - 140°C.

2:4:2'-trinitrostilbene - yellow needles, m.pt. 194 - 195°C.

2:4:3'-trinitrostilbene, m.pt. 183 - 184°C.

2:4:4'-trinitrostilbene - lemon yellow, m.pt. 240°C.

(All the above compounds from Thiele and Escales, Ber. 1901,34,2842).

2:4:6'-trinitrostilbene, m.pt. 156°C (Ullman, Ber. 1908, 41,2291).

2:4:2':4'-tetranitrostilbene - yellow needles, m. pt. 264-266°C(d.) (Green, J.C.S. 1908,93,1721).

2:4:6:4'-tetranitrostilbene - yellow needles, m.pt. 196°C (Ullman, loc.cit.).

2:6:2':6'-tetranitrostilbene - yellow needles, m.pt. 250°C (Reich. Ber. 1912,45,3060).

2:4:6:2'-tetranitrostilbene - brown needles, m.pt.181°C (Bishop and Brady, J.C.S. 1923,121,2367).

2:4:6:3'-tetranitrostilbene - yellow leaflets, m. pt. 159°C (Bishop and Brady, loc. cit.).

2:4:6:2':4':6'-hexanitrostilbene - yellow needles, m. pt. 211°C (Reich et alia, Ber. 1912,45,3060).

Nitrodibenzyls.

Although several workers have described the preparation of nitro derivatives of symmetrical diphenylethane, the literature records only two references to derivatives possessing more than four nitro groups.

Will (Ber.1914,47,704) states that 2:4:6:2':4':6'-hexanitrodiphenylethane is readily obtained by the direct nitration of 4:4'-dinitrodiphenylethane or by oxidation of 2:4:6-T.N.T in the presence of alkalies, but gives no preparative details or practical information beyond the fact that 2:4:6:2':4':6'-hexanitrodiphenylethane melts/

melts at 212°C.

Rinkenbach and Aaronson (J.A.C.S. 1930, 52,5040) studied the nitration of diphenylethane with the object of preparing 2:4:6:2′:4′:6′-hexanitrodiphenylethane. From one of their experiments on the nitration of 2:4:2′:4′-tetranitrodiphenylethane a compound m. pt. 209°C was isolated in small quantity and assumed to be identical with the hexanitrodiphenylethane described by Will (loc. cit.), attempts to prepare further quantities failed, however, even under the most favourable conditions for nitration. Prolonged sulphonation of 2:4:2′:4′-tetranitrodiphenylethane, prior to nitration, yielded alpha-2:4:5-trinitrophenyl-beta-2:4-dinitrophenylhydroxy-ethane.

Kharasch (J.A.C.S. 1921,43,2243) records the preparation of 2:4:2′:4′-tetranitrodibenzyl from 2:4:2′:4′-tetranitro-mercury dibenzyl without giving details and Wolff (Ber. 1913, 46,64) found that mercury dibenzyl similarly yielded diphenyl ethane. Attempts were not made to apply these methods to the preparation of hexanitrodiphenylethane.

Attempts to prepare hexanitrodiphenylethane by oxidation of T.N.T. in the presence of alkali were made by Rinkenbach and Aaronson (loc. cit.), using methods/

methods based on the work of Green, Davis and Horsfall (J.C.S. 1907,19,2079) but these were completely unsuccessful, Successful modifications of the existing methods for the preparation of 4:4′-dinitro and 2:4:2′:4′-tetranitro diphenylethane were developed, however, and improved yields obtained.

Attempts to Prepare 2:4:6:2′:4′:6′-Hexanitrodiphenylethane.

Attempts to prepare this compound from 2:4:6-trinitrobenzyl bromide in the presence of metallic sodium by the Wurtz-Fittig reaction were unsuccessful, and unchanged trinitrobenzyl bromide was recovered in quantity. 1 gm. (excess) metallic sodium was covered with dry ether and gently heated under reflux. 2:4:6-trinitrobenzyl bromide (6 gms.) dissolved in dry ether was gradually added and the mixture refluxed for 12 hrs. Precautions were taken to exclude moisture. 5 gms. trinitrobenzyl bromide were recovered together with a small quantity of a dark brown material m. pt. 200 - 240 °C (d.).

Higher temperatures were now employed, using copper powder as condensing agent (method of Ullman et alia). At temperatures of about 200°C ignition occurred, but when lower temperatures were employed (100 - 150°C) no reaction took place. Similar difficulties/

difficulties in the application of the Ullman reaction to the synthesis of polynitro compounds are recorded in the literature (J.A.C.S. 1930,52,2054,2070). When nitrobenzene was used as a solvent, at a temperature of 150-160°C, no reaction occurred.

In view of the statement by Will (loc. cit.) to the effect that dinitrodiphenylethane is smoothly nitrated to the hexanitro derivative, efforts were made to reproduce his results despite the failure of Rinkenbach and Aaronson (loc. cit.). In no case however, was hexanitrodibenzyl isolated. 4:4'-dinitrodiphenylethane was prepared by the method described by Rinkenbach and Aaronson (loc. cit.). 5 gms. dinitrodiphenylethane was dissolved in 25 cc. fuming sulphuric acid (20% free sulphur trioxide). 25 gms. of 95% nitric acid were added and the temperature gradually raised to 70°C and maintained there for 6 hrs. The reaction was cooled and poured on to ice. The product was collected, washed with water, dried and crystallised from toluene. It melted indefinitely at 220 -230°C (d.). Found C 43.0, H 2.3, N 12.7% but hexanitrodibenzyl requires C 37.1, H 1.8, N 18.6% .

E X P E R I M E N T A L

S E C T I O N.

Part III.

PREVENTION OF NON-ACIDIC BY-PRODUCT FORMATION.

PURIFICATION OF M.N.T.

CHAPTER 20.

EFFECT OF NITRATION MEDIA ON THE META CONTENT OF M.N.T.

It is generally excepted that in the nitration of toluene to M.N.T. about 4% meta isomer is produced, the proportion being only slightly influenced by temperature (p. 35). This work originally carried out by Van der Arend (p. 48) using excess of concentrated nitric acid, was confirmed for mixed acid by Gibson and collaborators (J.C.S. 1922,121,270).

This meta isomer represents a potential loss of alpha T.N.T. for in the trinitration process it is nitrated to unsymmetrical T.N.Ts. which require the use of buffered sulphite for their removal. Consequently, if an M.N.T. could be prepared containing no meta isomer substantial saving in costs would result.

A study of the literature (p. 48) suggests that altering the nitrating medium gives a M.N.T. containing little or none of the meta isomer. Moreover, an interesting claim is made by Klinsch (Austrian Patent, 15th. April 1909, 39581) that boric acid when added to nitric acid, renders cooling in the preparation of a mixed acid unnecessary. Furthermore it is claimed that in the nitration of hydrocarbons the /

the presence of boric acid results in the sulphuric acid taking up more quickly the water formed during the reaction, without the development of heat. If this be so, it is clear that the structure of the nitric or sulphuric acids must have been radically altered by the presence of this acid.

Accordingly, the following acids were investigated while the rate of formation and meta content obtained using these acids were compared with those of a 70% sulphuric, 4.5% nitric acids, 25.5% water.

(1) 70.2% sulphuric, 4.4% nitric acids, 25.4% water.

(2) 69.1% sulphuric, 4.7% nitric acids, 26.2% water, 0.3 gm. boric acid added for every 100 gms. acid.

(3) 68.9% sulphuric, 6.7% nitric acids, 26.4% water, 0.3 gms. boric acid added for every 100 gms. acid.

(4) 7.5 gms. boric acid added to 500 cc. acid (1).

(5) 69.0% phosphoric, 4.5% nitric acids, 26.5% water.

(6) 71.0% acetic, 4.7% nitric acids, 24.3% water.

(7) 92.5% dioxan (commercial), 7.5% nitric acid.

(8) 86.5% phosphoric, 4.1% nitric acids, 9.4% water.

(9) 91.6% acetic anhydride, 6.4% nitric acid, 2.0% water.

In experiment (2), the boric acid was added to the nitric acid then sulphuric acid and finally water. While no heat was liberated during the addition of the sulphuric acid to the nitric acid, much heat was liberated /

liberated on diluting with water. In experiment (3) the boric acid was added to the nitric acid and the cooled sulphuric acid - water mixture added. This was accompanied by little evolution of heat.

Mononitration was carried out as in chapter 25 (p. 194), using 45 cc. toluene and 400 cc. acid of the above acids, the temperature being maintained at 30°C. No nitration occurred in media 5,6 and 7, even on increasing the temperature to 65 - 70°C. With (8), the rate of reaction was very slow at 30°C. On increasing the temperature to 65°C, the rate was of the same order as number (1) acid. In (9) the samples were poured into an excess of water and the solution boiled to decompose the anhydride. The M.N.T. was sucked off, washed twice with cold water and dried. The refractive index of the samples, however, was not consistent and frequently denitration rather than nitration was indicated. The yield in (9) was particularly low and this is attributed to solution of the M.N.T. in the acid medium even on dilution. The M.N.T. moreover, was darker in colour. The results are expressed in table 25. Since acid (4) shows no increase in the rate of formation over (1), the increase in the rate of (2) and (3) is probably due to the slightly higher concentrations of nitric acid.

TABLE 25 /

TABLE 25. RATE OF FORMATION OF M.N.T. IN VARIOUS NITRATING MEDIA.

Acid	% M.N.T. after (mins.) 5	15	30	45	60	90	Remarks.
1	30.0	63.5	82.0	89.0	92.0	-	
2 and 3	36.4	69.5	89.0	93.5	93.5	-	
4	28.2	60.5	82.0	89.0	91.0	-	
5,6,7	No nitration occurred even on increasing the temp.						
8	5.1	9.1	21.8	59.0	78.5	93.0	Temp. increased to 65° C after 30 mins.
9	Nitration but no data for refractive index.						

DETERMINATION OF META CONTENT.

The method described herein, though longer than some, has the advantage over those described on p. 49 that in addition to giving the meta content of nitrotoluene it indicates to the manufacturer what grade of T.N.T. he can expect and the extent of the purification it will require. The M.N.T. is nitrated to the D.N.T. stage, washed and dried, further nitrated to the trinitro stage, washed and dried and a set point determined (cf. p. 78). The meta content is calculated from the graph on p. 81 and is shown in the table below.

TABLE 26. META CONTENT.

No.	Dry Set Point of T.N.T. °C	% Meta Isomer
1	78.75	3.8
2 and 3	78.53	4.4
8	78.17	5.1
9	79.20	3.0

These experiments show that the M.N.T. with the lowest meta content is obtained in acetic anhydride medium (No. 9), followed by sulphuric acid (No. 1). The cost and scarcity of acetic anhydride in this country rules it out and thus no advantage is to be gained by replacing the present system using sulphuric acid by any of the other methods described in this chapter.

Though it was not possible to alter the meta content of M.N.T. by the addition of boric acid to acid (1), it is possible to alter it by varying the temperature of mononitration as shown in the table below.

TABLE 27. EFFECT OF TEMP. ON THE META CONTENT OF M.N.T.

Author	Meta Content at ° C		
	30	50	60
Holleman, Proc.K.Akad. Wetensch, Amsterdam, 1908,11,248.	3.2		4.0
Holleman, Recc.trav.chim. 1914,33, 1	4.4		5.1
Ingold etc., J.C.S. 1931,1959.	4.4		
de Beule, Bull.Soc.Chim. Belge 1933,42,27	4.6		5.1

No doubt the amount and concentration of acid used plays an important part e.g. Gibson, (J.C.S. 1922, 121,270) found that change of temperature from 0 to 40°C using HNO_3 (Sp.G. 1.5) increased the meta content from 2.5 to 4.3. On the other hand, with a mixed acid of of composition 58.7% sulphuric, 23.8% nitric acids, 17.5% water /

water there was little or no change in meta content from 4.4% while with an acid of composition 64.5% sulphuric, 13.7% nitric acids, 21.8% water the meta content increased from 3.3 to 3.9% over the temperature range 0 to 40°C.

It was desirous to ascertain the conditions existing for acid (1). As nitration at 0°C is not feasible on a large scale, attention was focussed on the temperature range 30-60°C. Toluene was nitrated at 30 and 60°C using a 10% excess of acid in a nitration vessel akin to that of fig. 11 p. 78 for one and a half hours. Table 28 indicates the results.

TABLE 28. EFFECT OF TEMPERATURE ON META CONTENT.

Temp. C	% D.N.T. in M.N.T.	D.S.P. of T.N.T. °C	% meta isomer.
30	5	78.75	3.9
60	17	78.25	4.9

This table indicates that when the temperature is doubled the D.N.T. content of the M.N.T. is more than trebled, while meta content as calculated from p. 81 agrees with those of Holleman (loc.cit.). Since meta content is higher at 60°C than at 30°C, the final T.N.T. contains a higher percentage of unsymmetricals sufficient to lower the set point of the crude T.N.T. a further 0.5°C. To counterbalance this, the rate of nitration and ease of temperature control is easier at 60 than at 30°C.

CHAPTER 21.

ISOLATION OF o-, m- and p- M.N.T.

The effect of temperature discussed in the last chapter naturally leads one to investigate the physical methods which may lower the meta content of M.N.T.

It was suggested that fractional distillation might yield an M.N.T. free of meta isomer. This possibility was first of all treated from a theoretical point of view to see if the separation was practicable (section A) then from a practical point of view (section B).

SECTION A.

The normal boiling points of o-, m- and p- M.N.T. at atmospheric pressure are

o- 220.38; m- 231.87°C; p- 238.34° C.

The vapour pressures at low temperatures can be calculated from physical constants and values are given in Perry, Chemical Engineer's Handbook p.330 and are quoted in table 29.

TABLE 29. VAPOUR PRESSURES OF o-, m- and p-M.N.T.

Press. in mms.	10	50	100	200	300	400	500
b.pt. o-M.N.T.	90.0	130.0	152.0	174.0	188.0	199.0	210.0
b.pt. m-M.N.T.	100.0	140.0	161.0	181.0	194.0	205.0	214.0
b.pt. p-M.N.T.	100.0	140.0	164.0	187.0	201.0	211.0	220.0

FIG. 8

DUHRING DIAGRAM.

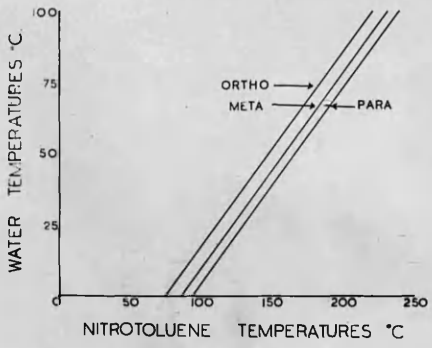


TABLE 29 (Contd.)

Press.	in mms.	600	700	760
b.pt.	o-M.N.T.	217.0	219.0	220.38
do.	m-M.N.T.	222.0	229.0	231.87
do.	p.M.N.T.	228.0	235.0	239.0

These figures suggest that while the lower boiling point of the ortho derivative is maintained, the vapour pressure of the other two (meta and para) approach one another and are identical below 100°C and therefore in the neighbourhood of this temperature meta could not be separated from para.

If the difference in the relative vapour pressures of the three derivatives can be maintained over a wide temperature range, however, then it might be possible to separate them by distillation. Making this assumption the relative volatilities may be represent--ed on a Duhring diagram as in fig. 8. where the line for o-M.N.T. is experimental and the other two lines are drawn parallel to this through their normal boiling points. From this chart at 130°C the vapour pressures of the three derivatives are: ortho - 49.7, meta - 31.0, para - 24.0 mm. mercury. (calculated from the vapour pressure of water at the appropriate temperatures.)

As the partial pressure of each is given approximately by the same formula

Pa/

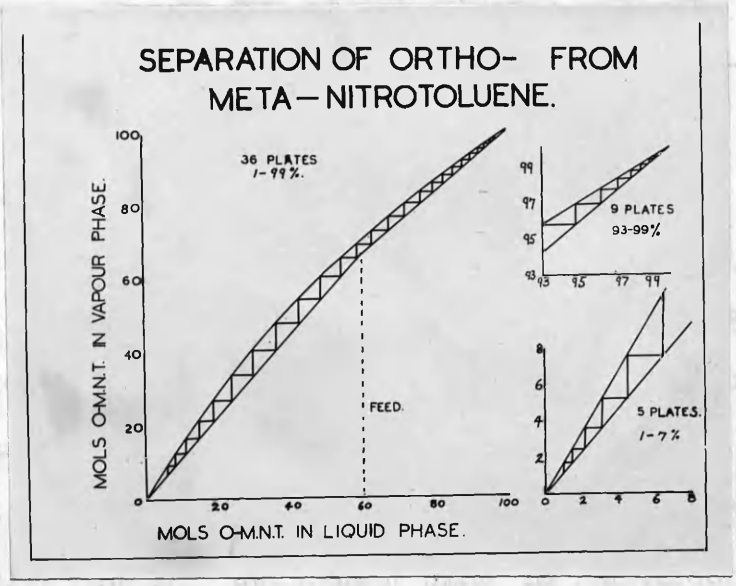

SEPARATION OF ORTHO- FROM META—NITROTOLUENE.
36 PLATES 1-99%.
9 PLATES 93-99%
5 PLATES. 1-7%
FEED.
MOLS O-M.N.T. IN VAPOUR PHASE.
MOLS O-M.N.T. IN LIQUID PHASE.

FIG. 17

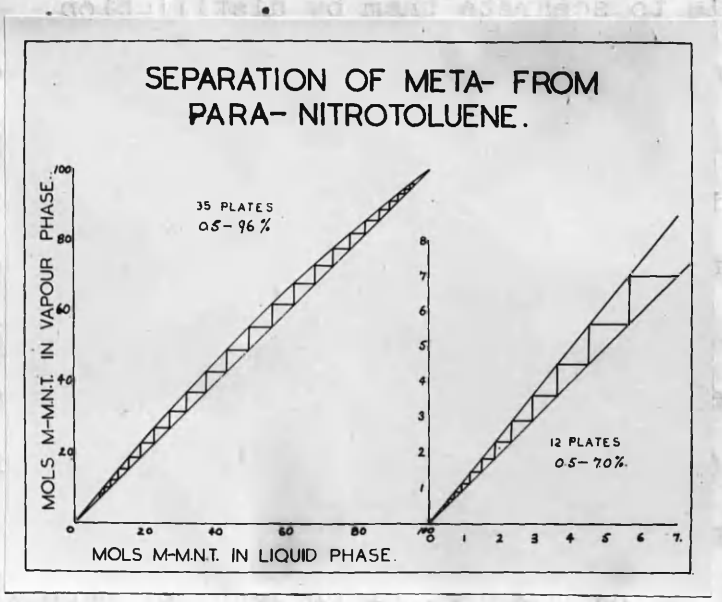

SEPARATION OF META- FROM PARA- NITROTOLUENE.
35 PLATES 0.5-96%
12 PLATES 0.5-70%
MOLS M-M.N.T. IN VAPOUR PHASE.
MOLS M-M.N.T. IN LIQUID PHASE.

FIG. 18

Table 30 . Data For Liquid-Vapour Equilibrium Curves in the Separation of O- from M- and P-M.N.T.

Mols. O-M.N.T. in Liq. Phase.	100.0	99.0	97.0	95.0	93.0	90.0	80.0	70.0	60.0	50.0	40.0	30.0	20.0	10.0
Mols. O-M.N.T. in Vap. Phase.	100.0	99.4	98.1	97.0	95.7	93.6	86.5	79.0	70.7	61.8	51.6	40.7	28.6	15.1
Mols. O-M.N.T. in Liq. Phase	6.00	4.00	2.00	0.00										
Mols. O-M.N.T. in Vap. Phase	9.08	6.27	3.55	0.00										

Table 31. Data For Liquid-Vapour Equilibrium Curves in the Separation of M- from P-M.N.T.

Mols. M-M.N.T. in Liq. Phase.	100.0	90.0	80.0	70.0	60.0	50.0	40.0	30.0	20.0	10.0	7.00	6.00	5.00	4.00
Mols. M-M.N.T. in Vap. Phase.	100.0	92.0	83.6	74.7	65.5	55.9	45.8	35.1	24.0	12.3	8.70	7.48	6.25	5.02
Mols. M-M.N.T. in Liq. Phase.	3.00	2.00	1.00	0.0										
Mols. M-M.N.T. in Vap. Phase.	3.76	2.52	1.26	0.0										

$$Pa = P.M.$$

where P is the vapour pressure of the pure substance and M is molar fraction of the pure substance present, equilibrium liquid-vapour curves may be constructed for any mixture. Tables 30 and 31 present the data for such curves.

For the purpose of distillation, it will simplify calculation to assume in the first place that the ortho derivative is to be separated from the meta-para mixture. This latter may be taken to have a vapour pressure equal to that of the more volatile (meta) fraction.

On the basis of these assumptions, a McCabe-Thiele diagram has been drawn up for the separation of the ortho derivative and is shown in fig.17. It will be seen that a high reflux ratio is chosen and that even with this some 40 theoretical plates will be required to produce 99% ortho, with an effluent containing less than 1%. The feed is taken to contain 60% ortho derivative and will enter on or about the 19th. plate from the top.

The residual mixture of meta and para derivatives will contain about 10% of meta compound, and fractional distillation of this is represented in fig.18. For this column a still higher reflux ratio (greater than 15) will be required but it should not be forgotten that the amount of product is small. The feed will/

will enter about the 12th. plate from the bottom of the column which will require a minimum of 35 plates to give a product containing 96% meta and a residue containing 99.5% para derivative.

Consideration of these two diagrams suggest that two separate fractionating columns will be required and that cost of both heat and plant will be high. The position might be improved if fractional crystallisation could remove the bulk of the para derivative from the mixture flowing from the base of the first column. The m.pts. of the two components are

meta 16.1°C and para 51.6°C.

It should be possible to crystallise out a fairly pure p-M.N.T., centrifuging it from the mother liquor. The mother liquor, richer in the meta derivative could then be distilled in a column of fewer plates with a lower reflux ratio.

SECTION B - PRACTICAL.

Distillation of commercial M.N.T. at ordinary pressures gives a dark coloured product and there is a tendency to explode towards the end of the distillation probably due to the presence of D.N.T. Distillation under vacuum (0.5 to 4.0 cms.) using columns 0.75 ins. diameter and up to 30 ins. high, is not successful. Furthermore, to prevent flooding it is necessary to

lag /

lag and heat the column electrically.

Using a short column 15 ins. long at 1 cm. pressure, commercial M.N.T. was separated into three main fractions (A) a portion b.pt. 72°C.
(B) a large portion b.pt. 72-76°C.
(C) p-M.N.T., b.pt. 77-8°C.

Attention is drawn to the small temperature range of 6°C between the boiling points of ortho and para compared with that at atmospheric pressure (cf. table 29, p. 161). Fractions (A) and (B) above were further subdivided by means of a Dufton column under a reflux ratio of about 5:1. The column was fitted with an aluminium spiral but no central glass rod as it caused too much entrainment. In addition the column was lagged and electrically heated.
(A) on further distillation gave (1) pure ortho C.P. -4.5°C. (2) a fraction of indefinite b.pt. which was added to (B). (3) crude para.
(B) on redistillation gave (1) pure ortho C.P. -4.5°C.
(2) a further fraction of indefinite boiling range.

No meta isomer could be isolated by distillation. It is to be noted that o-M.N.T. is assessed by taking the crystallisation point (C.P.) which is determined by freezing rapidly with solid carbon dioxide and noting the mean of temperatures when crystals separate and when they /

they disappear. According to literature (p. 37) the above C.P. would conform to the beta form.

From the foregoing, it would seem that the isolation of meta by distillation is not practicable on a large scale which bears out the data of figs. 17 and 18.

An attempt was made to alter the composition of the mixture by cooling the crude M.N.T. with solid carbon dioxide which resulted in a large amount of p-M.N.T. being frozen out. Distillation was now tried on the rich ortho - meta mixture with no success. The p-M.N.T. obtained from the above was purified by successive crystallisations from alcohol. The result of these experiments was to furnish (1) pure ortho C.P. -4.5°C. (2) crude ortho C.P. -5 to -6°C. (3) pure para, m.pt. 51.5°C.

As no meta M.N.T. could be obtained by distillation it was synthesised from p-toluidine by acetylation, nitration, hydrolysis, diazotis-ation and finally splitting off the diazo group (J.A.C.S. 1919,41, 1565). Pure meta, S.P. 16°C resulted. This was supplemented by a supply from B.D.H. Ltd., S.P. 15.25°C.

CHAPTER 22.

THE CHROMATOGRAPHIC ANALYSIS OF NITROTOLUENE MIXTURES.

Continuing to investigate physical methods of changing the meta content of M.N.T., as no data is available on the chromatographic analysis of nitrotoluene mixtures, work was undertaken in this field with a view to determining the scope of the method, which has proved so fruitful in separating isomeric substances (J.S.C.I. 1936,55,724; also Principles and practice of Chromatographs, Zechmeister and Cholnoky, translated by Bacharach and Robinson). In general, it was hoped to obtain a laboratory method for the separation (a) of alpha, beta and gamma T.N.Ts. (b) of m-M.N.T. from the ortho and para isomers and, if possible, to make the methods quantitative. Furthermore, if the analysis proved at all successful there was a possibility of replacing the expensive sulphiting process (p. 131) by an adsorption one. Moreover, fractional crystallisation of nitrotoluene mixtures frequently gives only partial separation with the final production of a eutectic. Chromatographic analysis, if workable, would solve this difficulty.

As an alternative to removing the unsymmetrical T.N.Ts.

T.N.Ts. from crude T.N.T., if m-M.N.T. could be adsorbed preferentially, even in part, to o- and p-M.N.T., the consequent saving of sulphite would prove of considerable value. Experiments were therefore carried out on (1) crude T.N.T. hot water washed and dried m.pt. 77.5-79.5°C. (2) eutectic mixture of beta and gamma T.N.T. m.pt. 79°C, obtained after the bulk of gamma T.N.T. had been fractionally crystallised from the T.N.Ts. derived from m-M.N.T. (3) eutectic mixture of 2:4 and 2:6-D.N.T. m.pt. 33°C, obtained after the bulk of the 2;4-D.N.T. had been fractionally crystallised from the D.N.Ts. derived from o-M.N.T. (4) commercial M.N.T., washed five times, once with 1% sodium carbonate, four times with water and dried over calcium chloride.

EXPERIMENTAL PROCEDURE.

Separation by chromatographic analysis depends on (a) width of column. (b) quality and chemical nature of adsorbent. (c) time of contact between adsorbent and material.

Adsorption Media: Inorganic adsorbents which are strongly acid or basic can be ruled out as may also dark or strongly coloured substances. The particle size should be about 2 to 10 μ. If the experiment has to be carried out with moist or aqueous solutions, the adsorbent /

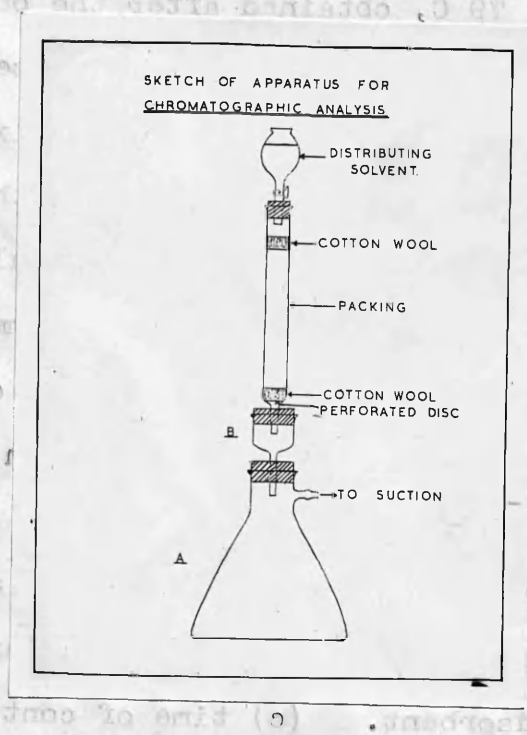

SKETCH OF APPARATUS FOR
CHROMATOGRAPHIC ANALYSIS
DISTRIBUTING SOLVENT
COTTON WOOL
PACKING
COTTON WOOL
PERFORATED DISC
B
TO SUCTION
A

FIG. 19

adsorbent must not fix nor swell in contact with water.

Solvent: Generally a solvent is chosen in which the material to be analysed is not too soluble, usually petroleum ether (b.pt. 60-80°C). As an eluent a solvent in which the material is very soluble is used. Numerous adsorbates are rapidly broken up by methanol, ethanol or acetone. It is not necessary to use pure solvent, however, 0.5 to 2.0% of solvent added to the distributing solvent, is sufficient.

With a coloured substance the bands can be observed. With a colourless substance, however, no bands can be seen though sometimes they can be observed under ultra violet light. In all the following cases, no bands were seen and consequently the adsorbates had to be washed down the column with eluents of varying composition.

Details of Method Employed - fig. 19.

A glass tube was pulled out at one end and fitted into a rubber stopper which in turn fitted into an adapter B connected to flask A. A perforated disc was dropped down the tube, followed by a pad of cotton wool to act as a support for the adsorbent. One of the specially prepared adsorbents was poured in, in small quantities, amounting in height to about 0.5 ins. Each small addition was lightly pressed down by means of a

glass /

glass plunger before the next addition. It is essential to have a uniform and well packed tube, otherwise channelling occurs. After all the adsorbent has been added, a final covering of cotton wool is put in to prevent disturbance of the surface.

Solvent, containing the material to be analysed, is poured down the tube (liquid being always retained above the cotton wool). Slight suction is applied to flask A - sufficient to give no more than a drop per sec. through the adsorbent. After the solution has percolated, the column is washed out with a solvent in which the substance is slightly more soluble e.g. if the distributing solvent be petroleum ether or say 10 parts of petroleum ether to 1 part benzene the mixture is developed by a solvent of composition akin to 3 parts petroleum ether and 1 part benzene.

(1) EXAMINATION OF CRUDE T.N.T.

Crude, unwashed, commercial T.N.T. was washed six times with water at 90 to 100°C then dried for six hours at 100°C. This product was too insoluble in petroleum ether (b.pt. 60-80°C) and consequently the T.N.T. was dissolved in benzene in the cold and the solubility reduced by the addition of petroleum ether.

The first adsorbent to be tried was aluminium oxide /

oxide specially prepared for chromatographic work by B.D.H. Though a separation of alpha from beta and gamma T.N.Ts. was effected, the use of this adsorbent was discontinued due to the formation of alkaline salts by the action of amphoteric alumina on the adsorbed T.N.T. rendering it red in colour.

Precipitated calcium carbonate, laboratory standard filter cel (a special kieselguhr), powdered silica, magnesium carbonate and magnesium oxide were all tried but gave no separation.

With Celite Analytical Filter Aid (a white kieselguhr), however, some success was achieved. A column of internal diam. 0.5 ins. and height of packing 8 to 10 ins. was employed. 2 gms. crude T.N.T. were dissolved in 35 cc. benzene, to which was added, after solution had been obtained, 50 cc. petroleum ether. After the solution had entered the column, it was washed down with solvent of composition 35 cc. benzene, 50 cc. petroleum ether. Each fraction, consisting of approximately 30 cc., was transferred to a distilling flask and the excess solvent distilled off, the residue being poured on to a watch glass and allowed to crystallise. The results with this adsorbent were as follows:

1st. fraction had m.pt. 80 - 80.5°C.

2nd. fraction had m.pt. 77 - 78°C.

3rd. /

3rd. fraction had m.pt. 74-77°C

4th. fraction had m.pt. 75-77°C

From these results, it is obvious that the alpha T.N.T. tends to pass through the column whereas the beta and gamma T.N.Ts. are retained and only appear as a eutectic in the final fractions. The cost of this adsorbent, however, precluded further experiments.

The results, however, were supported by experiments carried out using Fuller's Earth instead of Celite. Fuller's earth alone proved too fine and choked the tube. Consequently, attempts were made to overcome this by including ground pumice but with no success. Finally, A Fuller's earth - 10% Gooch asbestos packing was found which allowed the liquid to percolate slowly under suction. 2.5 gms. T.N.T. were dissolved in 50 cc. benzene and 60 cc. petroleum ether added. The wash solvent consisted of all distillates from previous experiments and would therefore be rich in petroleum ether. On passage down the tube

1st. fraction had m.pt. 80-80.7°C.

2nd. " " " 79.8-80°C.

3rd. " " " 64-70°C.

4th. " " " 70-71°C.

Since only about 33% yield of comparatively pure T.N.T. was obtained by this means, experiments were conducted on /

on a tube of wider diameter (0.75 ins. instead of 0.5 internal diameter) and height of adsorbent material 22 ins. On passage of 2.5 gms. T.N.T. in 50 cc. benzene and 60 cc. petroleum ether down the column the following results were obtained.

1st.	fraction	had	m.pt.	80-80.5°C
2nd.	"	"	"	80-80.5°C
3rd.	"	"	"	79.5-80°C
4th.	"	"	"	78-80°C
5th.	"	"	"	78-79.5°C.
6th.	"	"	"	73.5-78°C.

which shows a better separation.

To ascertain if the separation of alpha from beta and gamma T.N.Ts. was possible in the molten condition, washed and dried crude molten T.N.T. was mixed with aluminium oxide and kept in the molten condition, with occasional shaking, by heating on the water bath for two hours. The T.N.T. turned a deeper brown colour and the aluminium oxide became a dark pasty mass rendering filtration difficult. No difference in set point could be detected before and after this treatment. On replacing the adsorbent aluminium oxide by Norite, filtration was made impossible.

(2) EXAMINATION OF BETA--GAMMA T.N.T. EUTECTIC.

The previous experiments suggest that beta and gamma /

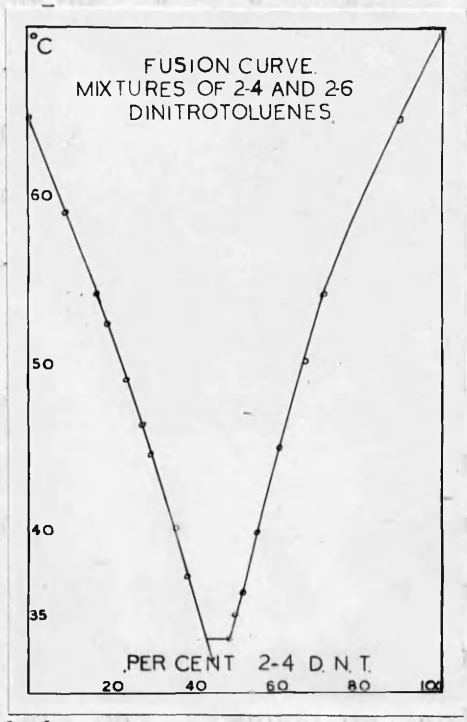

°C
FUSION CURVE.
MIXTURES OF 2-4 AND 2-6
DINITROTOLUENES.
60
50
40
35
PER CENT 2-4 D.N.T.
20
40
60
80
100

FIG. 20

gamma T.N.Ts. are preferentially adsorbed with respect to alpha T.N.T. Experiments, employing all the forementioned adsorbents on this beta-gamma eutectic have so far met with no success (cf. p. 40). No change in m.pt. could be detected after adsorption, confirming the results recorded in section (1).

(3) EXAMINATION OF 2:4 AND 2:6-D.N.T. EUTECTIC fig. 20.

The melting point of these two isomers are so near as to render identification difficult. From the D.N.T. obtained by the nitration of o-M.N.T., 2:4-D.N.T. is easily obtained by successive crystallisations from alcohol. No 2:6-D.N.T., however, is obtained, this forming a eutectic m.pt. 33°C with the remainder of the 2:4-D.N.T. This eutectic has so far defied attempts to break it up. Experiments with columns of 0.75 ins. internal diameter and height of adsorbent 11 ins. gave indefinite results and consequently the height of the adsorbent in the column was increased to 22 ins. 5 gms. of the eutectic were dissolved in 25 cc. benzene and 50 cc. petroleum ether added. The packing was Fuller's earth - 10% asbestos. The following were the results.

(1) m.pt. 64-68°C; after recrystallisation m.pt. 68-9°C

(2) liquid at ordinary temperature.

(3) /

(3) m.pt. 55-66°C: on recrystallisation m.pt. 62.5- 67°C. These results indicate that the eutectic can be broken up by the above means. The Fuller's earth has a greater affinity for the 2:6 isomer than the 2:4-D.N.T. which is, therefore, in the first fraction. The separation, however is long and tedious involving fractional crystallisation in addition to chromatographic analysis., though the latter treatment would probably suffice with smaller amount of eutectic. Experiments on the D.N.T. before the separation of the 2:4 isomer gave a wide range of melting points none of which could be associated with 2:6-D.N.T.

Lately, in Zeit. ges.Schiess u. Spreng. - Nitrocellulose, 1943,38,173 the separation of 2:4-D.N.T. from alpha T.N.T. was found to be practicable by chromatographic analysis using very small amounts of material.

(4) EXAMINATION OF CRUDE M.N.T.

Since in the above cases the adsorbent has the greater affinity for unsymmetrical compounds than for symmetrical constituents, it was considered possible that the adsorbent would have a greater affinity for the meta isomer (since it gives rise to the unsymmetrical compounds) than the corresponding o- or p-M.N.Ts. and thus permit of separation.

The /

The following experiments were carried out on M.N.T. treated as in paragraph (4) p. 168 and the M.N.T. from each was nitrated as on p. 78 and the set point of the final T.N.T. determined.

(a) 50 gms. M.N.T. nitrated, S.P. of T.N.T. 78.68°C.

(b) 70 cc. M.N.T. stirred 30 mins. with 5 gms. Fuller's earth, filtered and 50 gms. nitrated, S.P. of T.N.T. 78.68°C.

(c) 70 cc. M.N.T. heated and stirred at 75-85°C for 20 mins. with 13 gms. Fuller's earth, filtered and 50 gms. nitrated, S.P. of T.N.T. 78.6°C.

(d) 90 cc. M.N.T. passed through a column of Fuller's earth - 10% asbestos (tube 0.75 ins. internal diam.) with height of packing 10 ins. and 50 gms. nitrated S.P. of T.N.T. 78.6°C.

(e) 90 cc. M.N.T. passed three times through an alumina packing as above and 50 gms. nitrated, S.P. of T.N.T. 78.6°C.

These experiments show that M.N.T. is unaffected in composition by the adsorbents tried under the conditions specified therein. There was, however, a noticeable reduction in the intensity of colour of the M.N.T. in experiments (d) and (e) where column was used.

CONCLUSIONS. /

CONCLUSIONS.

(1) Alpha T.N.T. can be separated from beta and gamma T.N.Ts. by chromatographic analysis.

(2) The beta-gamma T.N.T. eutectic cannot be separated by the adsorbents used.

(3) The 2:4 - 2:6-D.N.T. eutectic can be partially resolved by chromatographic analysis. Fractional crystallisation, however, is necessary to complete the separation.

(4) The most suitable adsorbent for these purposes is Fuller's earth - 10% asbestos.

(5) M.N.T. cannot be separated by chromatographic analysis using the adsorbents specified.

(6) The adsorbents do not act preferentially as above, except on solutions of the mixture.

E X P E R I M E N T A L
S E C T I O N.

Part IV

ACCELERATION OF NITRATION PROCESS.

CHAPTER 23.

ACID ANALYSIS.

So far we have shown that little can be done to reduce oxidation losses or prevent the formation of beta and gamma T.N.Ts. It may be possible, however, to accelerate the rate of nitration without increasing the formation of by-products.

This section involves frequent acid analyses and consequently a chapter on the methods employed provides a suitable introduction. Attention in this chapter is focussed on the acid layer where in the case of a two phase nitration the nitrobody content is considerably below that of the nitrobody phase.

On the acid layer, analysis may be carried out on the cold slurry provided the acid/nitrobody ratio is high and/or the solubility of the nitrobody in the acid is not excessive. As nitrobody tends to occlude acid a better method of analysis is to have a homogeneous solution though an error is introduced depending on the bulk of the medium to be used to give homogeneity.

Two methods were initially employed for sampling laboratory nitration mixtures but latter, method (A) was discarded. (A)by drowning the acid layer in concentrated /

concentrated sulphuric acid, followed by precipitation of the nitrobody by dilution with water. (B) by drowning in concentrated sulphuric acid with no subsequent dilution - the nitrobody being in solution throughout the analysis.

METHOD **A.** Approximately 80% sulphuric acid (a concentration calculated to stop di and tri-nitration) was accurately standardised by titration against normal caustic soda using phenolphthalein as indicator. 80 gms. of this acid were weighed into a marked tared bottle fitted with a ground glass stopper. A 15 cc. sample was drawn from the nitrator into a small heated burette, allowed to settle then the acid layer transferred to the appropriate bottle. Immediately the sample had been added, the bottle was stoppered and well shaken to obtain the nitrobody in a fine state of division. When cold, the bottle together with the contents were weighed and 40 cc. distilled water carefully added with shaking. A considerable amount of heat was liberated and brown fumes were evolved which were incompletely dissolved. The bottles were cooled, reweighed and finally filtered through sinter glass crucibles under suction. The nitrobody was washed to remove adhering acid, (the washings being kept separate from the main bulk of the acid),

acid), then air dried till constant in weight. On each sample the following were done in duplicate.

(1) Total Nitrogen Acids (N.A.) by nitrometer expressed as percentage nitric acid and also as sulphuric acid.

(2) Total Acidity (T.A.) by titration expressed as percentage sulphuric acid.

(3) Total Oxidisable Matter (T.O.M.) by adding excess N/10 potassium permanganate and back titrating with thiosulphate. Result expressed as percentage nitrous acid.

(4) Urea Blank = Organic Oxidisable Matter, as in (3) after nitrous acid destroyed by urea. Result expressed as percentage nitrous acid.

(3) - (4) = true % HNO_2 = (a) % HNO_3.

(1) - (a) = % HNO_3.

(2) - (1) = % H_2SO_4.

METHOD B. The nitration mixture was drowned in 80% sulphuric acid for M.N.T. - D.N.T., up to 70% T.N.T. as before, but 85% sulphuric acid was used for the samples containing mainly T.N.T. The samples were then analysed without further dilution. Using this method it was possible to overcome errors involved in filtering and separating the nitrobody and what was more important, obtain a truer nitrous acid figure, since /

since using method (A) some was lost during dilution and filtering. The nitrobody was retained in solution through -out all determinations and was estimated by dilution with water, filtering, washing and drying, the filtrate being further extracted with ether.

ALTERNATIVE METHODS OF ESTIMATION.

Nitric Acid may be determined by the ferrous sulphate method of Bowman and Scott (Ind. Eng. Chem. 1915, 7,766).

Nitrous Acid. The method of Rupp and Lehmann (Arch. pharm. 1911,249,214) using acidified bromide - bromate solution gave reliable results but the oxidation was very slow. Chloramine T (van Eck, Pharm. Weekblad, 1926,63,1117) is quicker in its action though not so quick as potassium permanganate.

Nitrometer methods of estimation may be used where the presence of organic acid rules out the permanganate method e.g. Holden's urea method (J.S.C.I. 1930,49,220 T) gives reliable results.

$$CO(NH_2)_2 + 2\,HNO_2 = 2\,N_2 + CO_2 + 3\,H_2O$$

Amino sulphonic acid has been used to estimate nitrous acid in the nitrometer in preference to urea. In the case of absorption of nitrogen peroxide fume by 7 to 8% caustic soda, the method of estimating nitrite /

Nitrite was as follows. 10 to 20 cc. solution were introduced into the nitrometer and the cup rinsed with two successive water washes. Concentrated HCl was added to neutralise the solution then 10 cc. of a 2% aminosulphonic acid solution in water were added. After shaking the solution for a few seconds, 5 cc. 15% NaOH were added to remove carbon dioxide from carbonate present and the solution reshaken. After standing for a short interval the gas volume was measured.

A comparison of results obtained during absorption of nitrogen peroxide by NaOH in the cold according to the equation

$$2\ NaOH + 2\ NO_2 = NaNO_2 + NaNO_3 + H_2O$$

is given below

HNO_2 (expressed as HNO_3) By		HNO_3 by	Total Nitrogen acids as HNO_3 by
Amino Sulph. Acid	$KMnO_4$	$FeSO_4$	reduction to ammonia
0.17	0.19	0.17	0.36
0.90	0.90	1.07	1.93
1.24	1.24	1.44	

A volumetric method employing amino sulphonic is advantageous in the presence of large amounts of nitrobody (Analyst, 1943,68,273).

COMMENTS ON THE METHOD OF ANALYSES:

Due to dilution with sulphuric acid, any

error/

error in total acidity determinations of the drowned samples is multiplied five to seven times. Moreover, the sulphuric acid is obtained by difference and involves any error in the nitric acid determination. In cases of doubt a small sample can be taken for total acid determination without drowning in H_2SO_4. Using the H_2SO_4 dilution method, a check was made on the accuracy of the H_2SO_4 results as follows:

A mixed acid of composition 6% HNO_3, 3.6% HNO_2, 68.4% H_2SO_4 was taken and treated as below.

H_2SO_4 by difference from T.A. and N.A.	68.4%
H_2SO_4 by precipitation with $BaCl_2$ without removal of HNO_3 or HNO_2.	69.0%
Evaporation of HNO_3 + HNO_2 on a Petri dish at 100°C followed by titration after (a) 1 hr.	68.4
(b) 2 hrs.	68.3%
Heat at the boil 1 hr. followed by titration	74.1%
Steam distillation 1 hr. followed by titration	73.0%

These results show that the method of analysis is as accurate as the standard methods. Neglecting the last two results, the slightly high result in the second case is probably due to adsorbed $Ba(NO_3)_2$.

Considerable difficulty was experienced in obtaining concordant results with the nitrous acid figures /

figures in method (A) but steady and higher results were obtained using method (B). As illustrative of the effect of dilution on a nitrous acid solution, a simple experiment was conducted with a solution of nitrous acid in concentrated H_2SO_4 at ordinary temperature.

	% H_2SO_4	% HNO_3	Remarks
(1) Original	81.3	4.97	no brown fumes.
(2) Addition of 20 cc. water. Composition now	70.7	4.21	slight brown
Allowing for dilution: Original	81.5	4.87	fumes.
(3) Addition of a further 20 cc. water. Composition now	62.5	2.8	vigorous evolution brown
Allowing for dilution. Original	80.6	3.6	fumes.

The nature of the nitrobody may have a serious effect on the HNO_3 content and therefore indirectly on the H_2SO_4 content. e.g. if M.N.T. and to a less extent D.N.T. were present nitration would proceed on standing thus necessitating quick chilling and immediate analysis under such circumstances. This was illustrated by the following experiment in which two mixed acids of known strength were treated with (a) pure T.N.T. and (b) pure 2:4-D.N.T. The mixtures were treated on a water bath until the nitrobodies had dissolved, after which the solutions were cooled and analysed. The results are shown below:

(1) /

Table 32 . Nitration of 2:4 D.N.T. over 30 mins. - HNO_3 constant.

	Initial		15 mins. sample			Ratio acid to N./B.		30 mins. sample.			Ratio	
	Acid	slurry	Acid	Nitrobody	slurry	by wt.	by vol.	Acid	Nitrobody	Slurry	by wt.	by vol.
H_2SO_4	85.22	59.5	69.68	6.23	56.65	3.9	3.2	70.55	2.52	54.34	3.2	2.7
HNO_3	9.50	6.6	6.45	8.59	6.89			7.19	10.10	7.88		
HNO_2	1.29	0.9	2.66	0.65	2.45			3.27	0.73	2.66		
D.N.T.	-	30.2	12.35	51.50	20.39			8.80	42.96	16.93		
T.N.T.	-	-	4.41	31.78	10.03			4.71	40.77	13.29		
H_2O (diff.)	3.99	2.8	4.43	1.25	3.59			5.48	2.92	4.90		

	% H_2SO_4	% HNO_3
(1) Analysis of mixed acid.	84.5	10.6
4.17% T.N.T. added, analysis of acid.	84.3	10.4
2.60% D.N.T. added, analysis of acid.	84.6	9.9
(2) Analysis of mixed acid.	95.4	2.7
1.9% T.N.T. added, analysis of acid	95.0	2.8
1.6% D.N.T. added, analysis of acid	94.4	2.1

To emphasise the more important features of the nitration of D.N.T. to T.N.T., data for table 32 was collected during a laboratory nitration of 77 gms. 2:4-D.N.T. by 178 gms. of mixed acid of composition 85.22% H_2SO_4, 9.5% HNO_3, 1.29% HNO_2, 3.99% H_2O at 95°C. To eliminate a variable, the HNO_3 was kept constant. The amount added as 98% HNO_3 was determined by preliminary experiment to be 10 cc. over the first 15 mins. and 5 cc. over the second 15 mins. period. A sample was drawn at the end of 15 and 30 mins. into a heated burette, the respective volumes of acid and nitrobody phases after settling being noted. The acid phase was drowned in H_2SO_4 as on p. 180 while the nitrobody phase was treated as on p. 188. In both cases, T.A., HNO_3 by $FeSO_4$, HNO_2 and total nitrobody were estimated, the D.N.T. content being obtained from the washed, acid free nitrobody by gravity determination

The results are tabulated in table 32. This

table /

table shows the increase in HNO_2 with time due to the formation of oxidation by-products and the fact that D.N.T. is more soluble in mixed acid than T.N.T. Thus the acid always tends to carry the D.N.T. in solution, ensuring complete nitration but unfortunately also tending to increase oxidation losses. The nitrobody phase is shown to have an affinity for HNO_3. The chief characteristics of the nitration of D.N.T. are thus shown to be an affinity of HNO_3 by the nitrobody and an affinity for D.N.T. by the acid phase.

CHAPTER 24.

ANALYSIS OF THE ACIDS DISSOLVED IN THE NITROBODIES.

Following on from the last chapter, methods of analysing the acids dissolved in the nitrobody layer were investigated herein.

Preliminary tests were carried out on (a) undiluted samples. (b) samples drowned in water. (c) samples drowned in acetone. (d) samples drowned in 98% analar H_2SO_4.

It was found that (a) offered difficulties with nitrous acid and total acidity determinations. (b) had to be washed a further four times. The combined washings were suitable for total acidity determinations, but because of the excessive dilution, were not suitable for nitrometer estimations. (c) because of colour, proved of no value for all determinations. (d) offered distinct advantages.

It was decided to use the last method and as a check to take further samples by drowning in water. 98% H_2SO_4 was chosen as the diluting agent as it would reduce the dilution factor in addition to giving more accurate results.

The strength of the sulphuric acid to be used

was accurately determined. Tared ground glass stoppered bottles were filled with a known weight of the above acid - 30 cc. being taken for mono to di-nitration samples and 60 cc. for trinitration samples of about 10 cc. At the same time, tared bottles containing distilled water were prepared. Samples were taken as on p. 179.

The following are done in duplicate on each sample: (1) total acidity using phenolphthalein and occasionally methyl orange. The end point with the latter was on the average 0.2 cc. below the former; in all cases phenolphthalein end point was recorded. Either (2) nitrometer or (3) nitric acid by $FeSO_4$ (cf. p. 181.). (4) total oxidisable matter and organic oxidisable matter as on p. 180.

The following procedure was adopted for the diluted samples. The dilution liquor was poured off and a further quantity of distilled water added. The bottle was heated on the water bath till the nitrobody had melted when the contents of the bottle were thoroughly shaken then cooled with occasional shaking until the nitrobody had solidified. The acid water was decanted off and the process repeated a further three times, the total weight of the washings being noted and

a /

a portion used for determining the total acidity.

Results showed close agreement for HNO_3 by the nitrometer and $FeSO_4$ methods. The nitrous acid figures, however, were extremely difficult to duplicate. Furthermore a number of sulphuric acid results were negative (especially samples containing M.N.T.) while the same results obtained through water dilution were positive. This was attributed to "after nitration." Though this had been considered probable, it was believed that the low temperature of the samples would prevent such nitration but this was obviously not the case. It was therefore decided to drown the samples in 92% H_2SO_4 and allow as short a time as possible to elapse between sampling and the determination of total acidity and nitric acid values. For a 10 to 15 cc. sample, 60 cc. were taken for mononitration, 120 cc. for a dinitration and 150 cc. for a trinitration sample. In spite of the increased amount of equivalent 98% H_2SO_4 the trinitration samples solidified. In such a case where solidification occurred they were heated slightly on the water bath till solution was again obtained. Consequently $FeSO_4$ estimations for HNO_3 on trinitration samples proved more suitable than the nitrometer. The nitrobody was estimated as on p. 181.

If /

If more dilute acid were used for drowning, nitration would be inhibited but such large volumes would be required to obtain solution, that inaccuracies would inevitably occur.

Typical results showing the effect of "after nitration" on the nitric acid are given in example (1) and in (2) a similar effect is noted with H_2SO_4 figure.

	(1)	(2)
Organic Matter (% HNO_3)	1.96	1.55
True % HNO_3.	0.50	0.70
% HNO_3 by nitrometer	-	9.60
% HNO_3 by $FeSO_4$	7.45	9.80
"after nitration" effect 1 day	5.90	-
% H_2SO_4 by H_2SO_4 dilution	5.10	negative, "after nitration."
% H_2SO_4 by water dilution	-	5.0

Table 32, p. 185 shows the analysis of a nitrobody layer and illustrates the selective action of the nitrobody for HNO_3. It is natural to conclude that oxidation may be rife in such a case as this where HNO_3 is in excess of H_2SO_4. It was decided to examine the effect of maintaining nitrobodies saturated with acid at a fixed temperature and to ascertain if there was any change in set point with time. If nitration proceeded, it might be assumed that the set point would increase;

a /

a reduction in set point would indicate oxidation rather than nitration.

Accordingly, nitrobody at various stages in a nitration (No. 1 being rich in D.N.T., No. 2 richer in T.N.T. etc.) and kept at a temperature of approximately 80°C over a period of three to four hours without stirring. Samples were removed at intervals, washed thoroughly with boiling water and the wet set point determined (p. 79,81) using a 0 to 100°C thermometer. On keeping the nitrobody at the above temperature, it was noticed that the acid gradually separated from the nitrobody, indicating emulsion rather than solubility effect. Results are tabulated below:

Sample No.	Acid Separated after (mins.)	Wet Set Points after		
		5 mins.	2 hrs.	3 hrs.
1	45	49.0	50.0	48.5°C
2	2	33.3	38.5	39.0°C
3	10	58.5	60.0	60.0°C
4	30	71.0	71.5	71.5°C

From these results it can be seen that nitration occurs to a small degree especially in the D.N.T. regions. Oxidation to solid by-products if it occurs in the nitrobody phase is probably negligible.

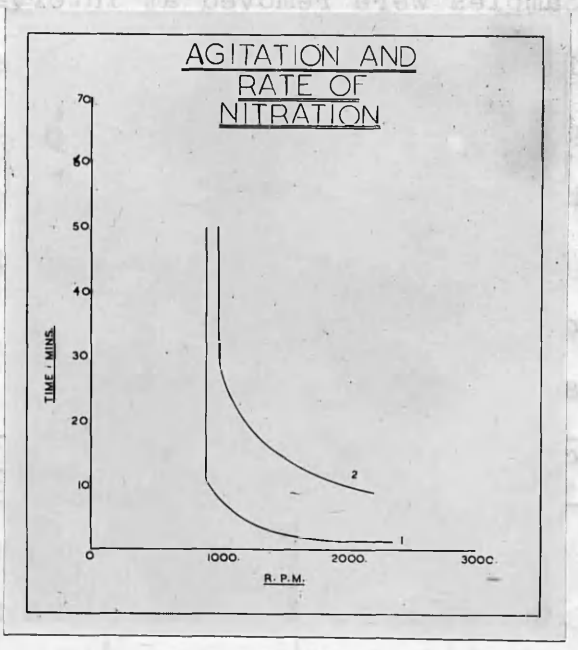

AGITATION AND
RATE OF
NITRATION
TIME : MINS.
70
60
50
40
30
20
10
0
1000.
2000.
3000.
R. P. M.
2
1

FIG. 21

CHAPTER 25.

CATALYSIS IN MONONITRATION.

Previous chapters have dealt with chemical and physical methods of reducing the meta content of crude M.N.T. none of which proved satisfactory. If the nitration process could be accelerated, time would be saved and an increased output result. The effect of by-products occurring in the spent acid from trinitration on the rate of mononitration was investigated to ascertain if any particular constituent impeded or accelerated the reaction.

Two methods were available for following the rate of nitration (1) noting the rise in temperature with time and (2) maintaining a constant temperature and following the course of the reaction by taking the refractive index of the nitrobody layer. Method (2) was preferred to (1) which introduced complications arising from the increased reaction rate at higher temperatures.

Preliminary experiments indicated the need for standardising agitation conditions in the nitration of toluene. Figure 21 indicates how the reaction rate varies with speed of agitation. Curve 1 is for an acid of composition 80% H_2SO_4, 5% HNO_3, 15% H_2O, curve 2 is /

is for an acid of composition 70% H_2SO_4, 5% HNO_3, 25% H_2O. There is obviously no point in carrying out a nitration if the stirrer speed (for this particular experiment) is lower than about 1500 r.p.m., for slight variations would result in large changes in the reaction rate. These curves were constructed using method (1) above but the same generalisations hold for the second method. Hence, before carrying out an experiment involving rate of reaction of a two phase system, it is advisable to draw the rate of reaction - R.P.M. curve and to chose the stirrer speed such that it lies on the horizontal part of the curve. In this particular case that would correspond to a stirrer speed in excess of 1500 r.p.m. Since this work was completed, McKinley and White (Amer.Inst.Chem.Eng. Trans. 1944,40,43) have shown the importance of agitation and have produced a curve identical with fig. 21.

Compounds which might possess catalytic activity investigated by other workers in the department, using the method outlined below were 3:5-dinitro-p- and o-cresol, halogens, primary secondary and tertiary alcohols, aromatic alcohols (nuclear and side-chain). Of these, the halogens (0.5 molar percentage on the toluene) in particular showed pronounced catalytic activity /

activity during the initial stages of the reaction but tended to the same ultimate figure in the same time as the blank experiment. All experiments were characterised by a rapid decrease in the rate of formation of M.N.T. with time. This was due to (a) M.N.T. formation decreasing contact between toluene and acid, (b) the decrease in nitric acid content with time (though a 5% excess was taken) and (c) dilution of the sulphuric acid by water produced in the nitration. It was considered possible, however, that the increasing production of nitrous acid might account for the falling off in the rate of formation towards the end of the reaction. In addition, the effect of substances likely to be present in the T.N.T. spent acid was investigated.

400 cc. mixed acid, composition 69.4% H_2SO_4, 5.0% HNO_3 were heated to 30°C and 45 cc. toluene added in bulk, the temperature being maintained at 30°C by an internal cooling coil. The toluene used had been distilled azeotropically (B.P. 536172 No. 28710/39) with methyl alcohol followed by fractionation. The final cut was washed with concentrated H_2SO_4, dilute alkali, water washed, dried and finally redistilled.

Samples of the slurry were drawn at 5 min. intervals and the rate of formation followed by refractometer. /

refractometer. The nitration was stopped at the end of 30 mins. after samples of the slurry had been withdrawn for HNO_2 content, a blank with urea being carried out to determine other oxidisable matter. Frequent blanks were carried through which indicated that the rate of agitation was constant. Table 33 summarises the results.

TABLE 33. EFFECT OF VARIOUS COMPONENTS ON THE RATE OF FORMATION OF M.N.T.

% M.N.T. after (mins.)					Compound added, Molar % on toluene.		Remarks.
5	10	15	20	30			
44.0	64.0	74.4	83.6	92.6	-		Blank
42.6	59.7	74.4	82.2	92.6	0.5%	trinitrobenzoic acid.	no catalysis.
45.5	63.0	74.4	82.2	92.6	0.5%	trinitro-benzaldehyde	do.
37.0	47.5	60.5	72.7	84.4	0.5%	by-product "A"	reaction retarded.
45.0	64.2	74.0	84.0	-	0.5%	3:5-dinitro-o-cresol	no catalysis.
48.0	66.3	75.1	86.1	-	1.0%	do.	slight catalysis.
50.0	68.0	77.9	89.8	-	2.0%	do.	definite catalysis.
54.8	71.2	83.6	88.1	94.1	0.5%	Nitrous acid	do.
53.2	73.6	85.1	91.3	96.0	1.0%	do.	do.

The compounds listed in the table, were all added to the acid before the addition of the toluene. In a previous experiment with another batch of acid, tetranitromethane /

tetranitromethane was found to have no effect on the rate of formation of M.N.T.

Nitrous acid determinations over the period of the experiment gave no indication of the rate of production. It was practically impossible to detect 0.5 molar per cent HNO_2 (calculated on the toluene) when dissolved in 400 cc. acid. Since nitrous acid (or rather nitrosyl sulphuric acid) was found to increase the rate of formation of M.N.T. from toluene, little importance was attached to these determinations. The nitrous acid solutions were made by adding the required amount of ice-cold liquid nitrogen peroxide to the mixed acid. This also involves the production of nitric acid (p. 12). Accordingly blanks were carried out after the addition of corresponding amounts of nitric acid to ensure that catalysis was not due to the slight increase in nitric acid content. The small addition of nitric acid, however, had no effect.

Catalysis was observed with 3:5-dinitro-o-cresol and nitrous acid. In view of the latter result, trial nitrations were carried out in the presence of a large excess of (a) urea and (b) amino sulphonic acid to ascertain if nitrous acid was essential for the initiation of nitration as is known in other nitration reactions.

The method was as before except that a portion of the /

the amino sulphonic acid (or urea) was added a few minutes before the addition of toluene. Thereafter, small amounts were added from time to time over 20 mins. In all, 6.86 gms. amino sulphonic acid and 6.34 gms. urea were added. The results are indicated in table 34.

TABLE 34. EFFECT OF THE ABSENCE OF NITROUS ACID IN MONONITRATION.

% M.N.T. after (mins.)				
5	10	15	20	Substance added.
44.0	64.0	74.4	83.6	Blank.
26.5	58.4	69.6	79.2	Urea.
15.4	59.9	67.3	76.6	Amino sulphonic Acid.

From these figures, it is obvious that the absence of nitrous acid in the nitrating acid does not prevent nitration taking place. When present, however, it has a decided accelerating effect on the rate of nitration of toluene to M.N.T. in the early stages.

CHAPTER 26.

RATE OF NITRATION OF D.N.T. CONTAINING 93% T.N.T.

The extent of purification required by crude T.N.T. is dependent on (a) specification, (b) D.N.T. content, (c) amount of unsymmetrical T.N.Ts. present which is governed by the meta content of the original M.N.T. It is (b) that one is concerned with in this chapter.

The rate of nitration of D.N.T. - T.N.T. is depicted by a graph similar to that of toluene - M.N.T. (p.158, 195; cf. also Ministry of Munitions, Tech. Recs. No. 2 p. 70). The time axis extends up to some four hours and the graph is characterised by a rapid fall off in the rate of formation of T.N.T. Experiments were conducted with three mixed acids, two of which were initially anhydrous, on a crude, water washed, dried T.N.T. containing 7% D.N.T. to ascertain (a) the times required to lower the D.N.T. content of T.N.T. to less than 0.1% D.N.T. (b) if it were beneficial to use anhydrous acids for the final stages of nitration. The acids used throughout had the following compositions - table 35.

TABLE 35. ACID COMPOSITIONS.

	Acid 1	Acid 2	Acid 3
H_2SO_4	100	96.45	91.0
HNO_3	4.76	4.56	4.8
H_2O	-4.76	-1.01	4.2

For /

TABLE 36. VARIATION IN D.N.T. CONTENT WITH TIME.

Acid	Time of Sampling hrs.	wet Set Point °C	% D.N.T.
1	0	72.9	7.10
	0.25	75.4	2.92
	0.50	76.06	1.82
	1.0	76.31	1.40
	1.5	76.71	0.74
	3.0	77.01	0.23
	4.0	77.10	0.08
2	0	72.90	7.10
	2.0	76.81	0.57
	3.0	76.91	0.40
	4.0	77.06	0.15
	6.0	77.06	0.15
	8.0	77.10	0.08
3	0	72.90	7.1
	0.25	75.31	3.07
	0.50	76.00	1.92
	1.0	76.66	0.80
	4.0	77.10	0.08

For each nitration the ratio of nitrobody to acid taken was 1:2 by weight. The nitrations were carried out in a closed unit having reflux condenser and stirring; the temperature used throughout all nitrations was 100°C. The nitrobody was first melted in the nitration flask and held at 100°C: the acid was then run in with stirring.

Each acid contained 4.5 to 5% HNO_3 but with varying amounts of H_2SO_4. No. 1 acid was anhydrous throughout while 2 contained water (due to nitration) at the end of the run. Using both these acids the nitrobody was completely soluble in the acid phase. with acid 3, however, two phases remained. The nitrobody was sampled by drawing off by suction at the appropriate time about 100 gms. slurry and drowning in cold water. The nitrobody was filtered, melted, washed with hot water then sulphited with buffered sulphite to maximum set point (p. 135) - gravity determinations proved too inaccurate to determine the low D.N.T. concentration.

The results are tabulated in table 36. It will be observed that in all cases after 4 hrs. of nitration the D.N.T. content is 0.1% or less and for minimum purification costs this is the time that would have to be adopted. The same curve is virtually produced by all three acids. All are characterised by a rapid fall during /

during the first half hour producing a reduction from 7.1 to 2.0% D.N.T.; the latter stages become very slow. There is little evidence from these experiments of any difference in nitrating power of the various acids. Thus, provided agitation is sufficient there is little need for employing anhydrous acids other than to obtain homogeneity where agitation is incomplete.

Since acceleration of the process both in mononitration and trinitration was unsuccessful it may be assumed that the by-products are unchanged.

CHAPTER 26.

SUMMARY OF WORK.

INTRODUCTION.

The introductory section discusses the history and mechanism of, together with the main factors governing, nitration. The nitration and the nitration products of toluene are singled out for special mention, especially with regard to their action with alkalies and sulphite, since they form the subject matter of this thesis.

EXPERIMENTAL SECTION - PART IA. GASEOUS OXIDATION LOSSES.

The modern tendency is to accelerate production. This may be done in the case of M.N.T. by increasing the temperature. Certain "evils", however, follow in the wake of such a step e.g. it was shown that the meta content of M.N.T. is increased (p. 160). Gaseous oxidation losses, though small compared with trinitration, are increased fourfold, volatilisation of toluene is more than doubled, 2:4-dinitrobenzoic acid is increased by some 60% over the temperature range 35 - 70°C.

Should M.N.T. contain free nitric acid, which is undesirable if the M.N.T. is to be stored, a suggested means of removal is to wash with 80% H_2SO_4 at 50°C which brings about dinitration at the expense of the /

the nitric acid. The resulting product is then further nitrated to T.N.T.

Gaseous oxidation losses in di- and tri-nitration are naturally higher than in mononitration but are shown to be little affected by acid composition, the total loss being about 3.5% carbon in the nitration of 2:4-D.N.T. to T.N.T. In-crease in temperature increases those losses, especially CO_2 which increases from 2.4% at 100°C to 5.2% at 130°C. The CO, on the other hand, tends to remain constant. The D.N.Ts. were shown to be primarily responsible for the large loss of carbon, the unsymmetricals showing a greater loss than 2:6- which in turn, was greater than 2:4-D.N.T. The T.N.Ts., on the other hand are shown to be comparatively stable to oxidation to gaseous products by mixed acid. Gamma T.N.T., in contrast to alpha and beta T.N.Ts. suffer little gaseous loss, yet including solid oxidation by-products the losses incurred by both beta and gamma are in excess of those incurred by alpha T.N.T.

PART IB. ACIDIC BY-PRODUCTS.

There is little likelihood of toluene sulphonic acids being formed in the nitration of toluene. Should this occur, they are extremely stable. Moreover, the mechanism of nitration, wherein a nitro group replaces the sulphonic acid group is shown to be untenable in this case under /

normal nitration conditions. Older theories of nitration by mixed acid postulate the intermediate formation of sulphonic acids.

Of the isomeric M.N.Ts., p-M.N.T. is shown to give the purest alpha T.N.T. and by nitrating mixtures of the three isomers a graph was provided correlating wet and dry set points of the final T.N.T. with the percentage of m-M.N.T. This enables the percentage of unsymmetricals (T.N.Ts.) to be calculated as distinct from acidic impurities. On renitrating each of the T.N.Ts. from the three isomeric M.N.Ts., that from p-M.N.T. gives a small amount of a by-product, designated "A" which appears to be inhibited by the presence of 2:6-D.N.T. A suggestion that "A" may be trinitrobenzoic acid anhydride is disproved while the formation of trinitrobenzene is shown to be possible if trinitrobenzoic acid is present.

By-product "A" is shown to be a dicarboxylic acid pictured as being formed by the union of two trinitrobenzaldehyde molecules through nitrogen via the isomeric 2-nitroso-4:6-dinitrobenzoic acid as detailed on p. 113. The 2-nitroso-4:6-dinitrobenzoic acid was prepared in what appeared to be rather an impure form and was shown to yield "A". The nitroso acid has, however, yet to be isolated from nitration slurries. "A" has also been synthesised /

synthesised from 2:4:6-trinitrobenzaldehyde but the demarkation line between conditions favouring the formation of trinitrobenzoic acid or 'A' is very slight.

2:4:6-trinitrobenzaldehyde is shown to be more stable than 2:4-dinitrobenzaldehyde towards mixed acid and that at temperatures up to 85°C both are unbelievably stable. The oxidation of these aldehydes, moreover, is inhibited by the presence of nitrobody, especially 2:4-D.N.T. On the other hand, 2:4-dinitrobenzaldehyde is more stable towards 85% H_2SO_4 than 2:4:6-trinitrobenzaldehyde.

Dinitrocresols are shown to be absent as they are oxidised in the presence of HNO_3 at temperatures greater than 40°C. 2:4-dinitrobenzoic acid is found to the extent of about 0.9% in the spent acid. Examination of the crude T.N.T. shows the presence of 1.5 to 2.0% acidic organic matter in the form of a red jelly which was assumed to be 2:4-dinitrobenzoic acid because of its equivalence on titration with alkali. A method of estimating 'A' in the presence of trinitrobenzoic acid was evolved during these tests.

Part II. REMOVAL OF NON ACIDIC BY-PRODUCTS - PURIFICATION OF CRUDE T.N.T.

The difference between wet and dry set points is 3.5°C though in working with crude T.N.Ts. a difference of 3.65°C is more common due to the presence of other impurities /

impurities e.g. tetranitromethane. A drying time of 4 to 6 hours is required to convert a wet to a dry set point.

The removal of the unsymmetrical T.N.Ts. is accompanied by an alpha T.N.T. loss which is dependent on the rate of agitation, pH of the solution, temperature and concentration of the solution. Using a solution of composition 4% Na_2SO_3,7 H_2O, 0.8% H_3BO_3 to sulphite a synthetic crude T.N.T. at 80°C, each wash lasting 30 mins., the average loss entailed by one sulphiting followed by three water washes is 2.5%. 2:4- and 2:6-D.N.Ts. were found to be stable to sulphite solution and consequently it was possible to determine the D.N.T. content of a crude T.N.T. by sulphiting the mixture with buffered sulphite to maximum set point to remove the unsymmetrical T.N.Ts.

The mechanism of the action of alkali on alpha T.N.T. proved extremely complex and resolved itself, unsuccessfully, into attempted synthesis of hexanitro-stilbenes and -dibenzyls for comparison purposes.

PART III. REMOVAL OF NON ACIDIC BY-PRODUCTS - PURIFICATION OF M.N.T.

Attempts to reduce the 4% meta isomer in commercial M.N.T. naturally occupies a major portion of this section. The literature shows that the temperature of nitration and the nitration media are critical. In practice /

practice, temperatures below 30°C are unsuitable. On the other hand, in the case of an acid of composition 70% H_2SO_4, 4.5% HNO_3, 25.5% H_2O, doubling the temperature from 30 to 60°C increases the proportion of meta isomer by 1%, thus increasing the degree of purification required by the crude T.N.T. Altering the nitrating media, however, has little effect. With regard to physical methods, chromatographic analysis was found to be unsuitable while exhaustive fractional distillation yielded an ortho and para M.N.T. free from meta isomer. None of these methods can compete with the present method of nitration and therefore separation of meta from ortho and para M.N.T. though possible, is not a practical proposition.

Part IV. ACCELERATION OF NITRATION PROCESS.

Acid analyses provide the introduction to this section. Using suitable methods it is shown that in the two phase nitration of 2:4-D.N.T. the nitrobody has an affinity for HNO_3 whereas the acid tends to extract preferentially 2:4-D.N.T. The end stages of the above nitration are shown to be very slow and little advantage is to be gained (if agitation is efficient) in using anhydrous acids.

The rate of agitation in a two phase nitration system is important. A method of obtaining steady conditions /

conditions by working above a certain speed, and the catalytic effect of nitrous acid in the early stages of the nitration of toluene are emphasised.

Since efforts to accelerate the nitration process proved of little avail it is unlikely that any modification of the existing method, along lines suggested in this section, will affect the rate of formation of by-products.

SAMPLING UNIT

FIG. 9.
(p. 40)